Dynamics of Charge and Spin Excitations
in InGaAs/GaAs Quantum Dots

PROEFSCHRIFT

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The equations on the cover form a 4 level rate-equation model of the evolution of excitons in quantum dots, including the hyperfine-mediated exchange of angular momenta with the nuclei of the dot.
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Chapter 1:

Introduction

1.1 Introduction to semiconductor quantum dots

Semiconductor heterostructures provide a means to restrict the movement of charge carriers and electromagnetic fields in electronic and optoelectronic devices. In the high-electron-mobility transistor, for example, charge donating impurities are introduced to a high-bandgap semiconductor, grown adjacent to a lower bandgap material, into which the donated carriers inevitably relax. This means that during device operation the carriers flow in a high-purity crystal, with minimal scattering, enabling very high frequency switching. In semiconductor laser technology, the use of a double heterostructure, providing both carrier confinement and optical waveguiding, was the crucial step allowing lasing at currents low enough to prevent the device destroying itself almost immediately when switched on. Devices such as these, relying completely on high quality interfaces between disparate semiconductor materials, are now so ubiquitous in our modern information-processing technology that if they were all to be removed from the planet overnight, it would drastically change the lives of a great portion of the people on Earth.

A new engineering freedom is realized when the dimensions of semiconductor heterostructures are reduced to something of the order of the charge carrier de Broglie
wavelength. When this is done, the usual quasi-continuous bands of available electron states become replaced by discrete energy levels, leading to new possibilities, such as conduction that is limited to specific carrier energies, for example in the resonant tunneling diode, and discrete optical transitions, leading to enhanced optical gain in lasers and amplifiers, size-tunable emission/detection wavelengths, emission with high spectral purity, and improved thermal stability.

The ultimate implementation of this form of scale engineering is when the size reduction is performed on all three spatial dimensions, leading to complete energy quantization, and a density of states resembling a sequence of delta functions. Small structures employing this three-dimensional confinement are termed quantum dots. A further advantage of such complete energy discretization is the possibility of very long dephasing times for coherent processes, such as those involving the spins of charge carriers. The race is now on in the semiconductors research community to find good ways of utilizing this latter benefit, in highly non-classical technologies, such as quantum key distribution and quantum computation.

One can appreciate the approximate size a heterostructure should be in order to match the electron wavelength by invoking the de Broglie relation:

\[ \lambda = \frac{h}{p} \]

where \( \lambda \) is the de Broglie wavelength, \( h \) is the Planck constant, and \( p \) is the electron momentum,

\[ p = \sqrt{2m^*E} \]
where $m^*$ is the electron effective mass and $E$ is its kinetic energy. If we choose for the energy that of the majority of electrons in the material, then we can assume that

$$E = \frac{3kT}{2},$$

where $k$ is the Boltzmann constant and $T$ is the absolute temperature. Rearranging for the wavelength gives

$$\lambda = \frac{h}{\sqrt{3m^*kT}}.$$  

Considering GaAs, which has an effective mass of 0.067 $m_0$, and assuming room temperature operation, we arrive at a length of about 25 nm. Clearly the production of semiconductor structures on this scale in all three dimensions poses a major challenge.

Using semiconductor growth techniques such as molecular beam epitaxy (MBE) and metal-organic vapour phase epitaxy (MOVPE), which permit the build up of material atomic layer by atomic layer, it is possible to reduce the problem of producing three dimensional objects of nanometer scale to one of precise control of the growth in only one dimension. Such a process is called self assembly of quantum dots, and a common example of self assembly is the Stranski-Krastanow growth mode. In this process, the difference in the lattice parameters of two semiconductors grown one on top of the other is small enough that the upper material initially assumes exactly the crystal arrangement of the material below. Because the upper material has a higher preferred atomic spacing, however, a compressive strain accumulates in the crystal, which after only a few atomic layers, leads to relaxation by the formation of many small islands bulging upwards. These quantum dots are typically a few tens of nanometers wide and a few nanometers high, leading to quantum confinement of carriers in three dimensions and complete
discretization of the carrier energy levels. A very common material system used for this process is InAs grown on GaAs. The InAs dots are normally covered in a further layer of GaAs, enhancing greatly their optical properties. It is the study of these InAs/GaAs quantum dots grown by MBE that is the preoccupation of this thesis. With doping of the host material, these buried quantum dots can also be populated electrically.

1.2 The study of individual quantum dots

Typically, when self-assembled quantum dots are analyzed spectroscopically, one observes a broad band of optical transitions, which does not reflect the atomic-like properties of a system exhibiting quantum confinement in three dimensions. This fact arises from the range of sizes, geometries, and compositions present in an ensemble of dots due to the non-deterministic nature of the growth process, and special measures must be taken in order to isolate a single quantum dot.

In order to study an individual quantum dot, the growth process must be optimized to give a low enough dot density, something not much higher than $10^9$ cm$^{-2}$ being typically suitable. The growth must also be sufficiently well controlled to provide a high enough optical quality for the signal from a single dot to be measurable. Furthermore, unless the dot density is extraordinarily low, areas of the sample, typically a few hundred nanometers across must be isolated, often by etching of the surrounding material or by masking with a patterned layer of an opaque metal.

Marzin et al.\textsuperscript{1} were one of the first, in 1994, to observe the photoluminescence of individual quantum dots. This was achieved by the etching of square mesas a few hundred nm wide. When the mesas were studied, the usual inhomogeneously broadened spectrum was replaced by a large number of very sharp lines, no broader than the system
spectral resolution. The authors of this work were able to confirm that the spectral lines were indeed from the dots, and not from defect states introduced by the etching process, when a histogram of the number of lines observed at different emission energies in several mesas reproduced almost perfectly the original quantum dot spectrum obtained from the unpatterned sample.

In the simplest case of luminescence from a single dot, one sees a spectrum consisting of a single sharp line resulting from the recombination of an electron-hole pair occupying the ground state, termed a single exciton. The term ‘exciton’ is used imprecisely here, as often there may be no excitonic binding present, but it is used here to denote an electron-hole pair in a dot to remain consistent with its almost ubiquitous application in the literature. If the rate of generation of electron-hole pairs is higher, one can expect to see additional emission lines, due to recombination from multi-excitons or charged excitons. The biexciton, for example, consisting of two electron-hole pairs of opposite spin, both occupying the ground state of the dot, emits at an energy modified relative to that of the single exciton, due to the Coulombic interaction between the four charges. The binding energy of the biexciton is governed by a range of factors and can be either positive or negative.

Brunner et al. observed a photoluminescence (PL) spectrum from an ensemble of dots formed as thickness fluctuations in a quantum well, for which the number of sharp emission lines increased as the pump power was raised. They produced a simple theoretical argument that the intensity of the single exciton should grow linearly with the pump power, and that the biexciton should grow quadratically with power. Their experimental results matched very closely this prediction. Landin et al. reported more complex spectra from individual dots, with extra lines due to charged excitons, that is, a single electron-hole pair recombining in a dot also occupied by an additional unpaired charge, either positive or negative.

A single exciton in the ground state of a quantum dot is expected to exhibit non-classical light emission, just like that of a single atom. Provided the exciton line can be
spectrally isolated from all other emissions, the probability for 2 photons to be emitted at exactly the same time vanishes, due to the fact that having just emitted, there is a finite time required for another electron hole pair to occupy the quantum dot. Thus, an isolated quantum dot can be used as a single-photon emitter, which accounts for a great deal of the interest in the optical properties of such an entity. A single-photon emitter, for example, can be used as a light source for quantum key distribution (QKD), which enables a form of encrypted data transfer that is mathematically guaranteed to be secure.

Even greater interest in isolated quantum dots was sparked by proposals such as that of Benson et al.\textsuperscript{4}, which built further upon the idea of the quantum dot as a single-photon emitter, by suggesting that a light emitting diode with a single dot as its active medium could be used to produce pairs of photons exhibiting quantum entanglement. The authors described a means based on resonant electrical population of the dot to generate bi-excitons, each electron pair of which would act as a single-photon emitter. Furthermore, due to the Pauli exclusion principle forbidding 2 electrons of the same spin to occupy the same atomic state, and the one-to-one conversion of the spin of the charge carriers into the polarization of the emitted photons in quantum dots, these pairs of photons can be expected to show a high degree of polarization entanglement – if we know the polarization of one the photons, we know that of the other, without having to measure it, since the Pauli blockade prevents the remaining electron-hole pair from having the same spin state. This, of course, relies on the assumption that the spin-flip time of the quantum dot exciton is much longer than the carrier recombination time. Entangled pairs of photons can be used in advantageous schemes for QKD, and are also essential for many proposed quantum logic devices, which can be considered an area of research offering not only highly challenging intellectual pursuit, but also the possibility of great practical benefits in the field of large-scale computation.

In fact, it can be considered that the threat of quantum computation being realized is a major stimulant of the interest in QKD, as the current public-key encryption strategies, such as the RSA algorithm, rely on the fact that almost no conceivable
classical computer can perform the calculations needed to decipher an intercepted message, while quantum computers would be expected to excel at exactly this kind of calculation.

Other applications for emitters of entangled photons can be found in other quite different fields, such as optical lithography. Market forces and the historical trends in the development of microchip technology, collectively referred to as Moore’s Law, suggest that the size of integrated circuit elements should be reduced by half every year or two. An obvious problem with this forecast is that optical lithography, the standard technology for tracing the layout of circuit elements on a chip, as currently implemented must eventually succumb to the diffraction limit, by which is meant that features smaller than half the wavelength of the light used for tracing can not be created. If, however, as Boto and co-workers suggest, the lithographic process were adapted to make use of entangled photons, it would become possible to reduce feature sizes beyond the diffraction limit. It is argued that if the number of entangled photons is \( N \), then the minimum achievable feature size becomes \( \frac{\lambda}{2N} \).

Isolated self-assembled quantum dots are not the only systems capable of producing single photons. For example, single atoms, ions, molecules, crystal defects in diamonds, and colloidal quantum dots (discussed below) have all been used to demonstrate single-photon emission. A quantum dot, embedded in a solid semiconductor material, however, offers several significant advantages over other single-photon emitters, both in terms of fundamental experiments and possible practical devices. Experiments with single atoms or ions require substantial effort to hold them in place, while isolating them from their environment, which ceases to be a difficult problem with dots inside a semiconductor. With non-resonant optical excitation of self-assembled dots, absorption is not limited to the dot itself, but efficient carrier capture from the host material greatly enhances the pump efficiency. Similar reasons, coupled with the ability to gate semiconductor structures make it also possible to achieve single-photon emission electrically. The maturity of semiconductor processing technology makes it relatively
straightforward to implement designs for practical devices. Furthermore, while all other emitters tend to produce photons equally in all directions, the fabrication of semiconductor dots inside micro cavities allows great control over the directionality of the emission, and hence the collection efficiency. Other advantages of self-assembled dots include the usually high splitting for multi-particle states in self-assembled dots due to tight carrier confinement, and the normal absence of deleterious effects such as bleaching and blinking.

The first experimental verification of the single-photon emission from a spatially and spectrally isolated quantum dot came from Michler et al., in the year 2000\textsuperscript{11}. The method used time-correlated single-photon counting to measure the second-order correlation function for the optically-pumped colloidal CdSe/ZnS quantum dot. The

![Figure 1.1: Histogram of photon coincidences for a CdSe/ZnS quantum dot (lower curve) showing a strong antibunching signature. Also plotted is the histogram for a cluster of dots (upper curve), which serves as an experimental control. Reproduced from reference 11.](image-url)
single-dot PL was divided at a beam splitter and passed to two photo-detectors, allowing a histogram of the number of coincidences of the two detectors to be plotted as a function of the time delay between the two arriving photons. This histogram can be shown to be proportional to the second-order correlation function for the emitter. The authors observed a strong suppression of the number of coincidences at zero time delay, relative to the number at time delays much longer than the exciton recombination time, which is taken as proof that the photons are emitted one at a time, and not in pairs or larger bunches. The recorded histogram of photon coincidences, plotted as a function of the time delay between arrivals at the two detectors is reproduced in Figure 1.1. The upper measurement in the figure shows a control measurement, using the luminescence from a cluster of several quantum dots, for which no antibunching is expected.

The first demonstration of antibunching with dots inside a solid host material was performed by Zwiller et al.\textsuperscript{12} who obtained a similar histogram for an isolated InAs/GaAs quantum dot. The measurement was fitted by a simple exponential model,

\[ I = a - be^{-\frac{t}{\tau}} \]

allowing the exciton emission time constant, c, to determined. The fitted value for this emission lifetime was 740 ps.

Michler et al.\textsuperscript{13}, in 2000, were able to demonstrate a high degree of photon antibunching from an isolated self-assembled InAs quantum dot under pulsed optical excitation, creating the first proof of a triggered single-photon source. The histogram of coincidences in this case appeared as a sequence of pulses separated by the period of the pulsed laser used for excitation. The peak plotted at zero time delay, however, had an area only 12\% of that of the other peaks, indicating the single-photon character of the emission.
It wasn’t long before researchers started reporting successful antibunching experiments on QD emission lines other than the uncharged single exciton. In one such work, three emission lines from an isolated dot were studied using time- and power-dependent measurements, and were identified as the single exciton, a charged exciton, and a biexciton. All three lines exhibited strong antibunching when subjected to photon correlation measurements. According to a simple model, the biexciton, having two electron-hole pairs that might decay at any moment, is expected to exhibit an emission lifetime roughly half as long as the exciton. This was confirmed by the time resolved measurements, and also reflected in the antibunching experiments, performed using a pulsed laser pump. The linewidth of the coincidence peaks observed in the correlation measurements was much narrower for the biexciton than for either of the other two transitions, indicating that the biexciton can be used as a single-photon emitter with much reduced timing jitter.

In 2001, it was shown that photon correlation measurements could be used to demonstrate cascaded emission from a dot containing two excitons. Here, the PL from an isolated dot was passed to a beam splitter, and then to two monochromators, one tuned to the exciton emission wavelength, and the other tuned to the bi-exciton resonance. Single-photon detectors placed behind each monochromator were used to trigger a time correlator circuit. By triggering the correlator to start using photons from the biexciton and to stop using photons from the exciton, the histogram of coincidences proved the presence of a cascaded sequence of emissions. Since the emission of the biexciton leaves the dot still populated by the exciton, there was a strong enhancement of the coincidence rate for small positive time delays. Strong antibunching was seen however, for short negative time delays, due to there being no transition that could emit immediately before the biexciton. The correlation function that was reported following this work is reproduced in Figure 1.2.
Figure 1.2: Cross-correlation between quantum-dot exciton and biexciton, measured by Moreau et al. The left-hand vertical axis shows the calculated second-order correlation function. The strong enhancement of the coincidence rate at time delays immediately after zero is a consequence of the high probability for the exciton to emit after the biexciton decays. The suppression at small negative time delays results from the impossibility for the biexciton to emit immediately after the exciton.

Kiraz et al.\textsuperscript{16} performed similar cross-correlation experiments, as well as auto correlations, for several different lines emanating from a single dot, and were able to identify the exciton, biexciton, and charged exciton, from the particular asymmetry of each cross-correlation histogram. The exciton and the charged exciton, for example, do not form partners in a cascade process, and therefore do not exhibit the kind of coincidence enhancement seen for the biexciton and exciton, but their cross-correlation did exhibit a faster rise from the antibunching dip to the background coincidence rate on one side of the histogram, compared to the other. This is seen as a consequence of the faster emission from the charged exciton, as there is no dark state for this configuration. Carriers were excited non-resonantly in the dot and it is therefore possible for a single
exciton to have spin of ± 2, in which case there is a necessary delay before emission, while the exciton waits for one of the spins to flip.

All the experiments discussed so far have featured optical excitation of quantum dots, but for practical applications one can readily see the advantages of achieving carrier injection by electrical means. Such a scheme, capable of single-photon emission, appears in the literature for the first time due to the efforts of Yuan and co-workers\textsuperscript{17}. Growth of the quantum dots in the intrinsic region of a $p$-$i$-$n$ diode made it possible to pass a current through the dot. The top electrical contact also served as a mask with narrow apertures, to facilitate the isolation of a single dot. The usual time-correlated single-photon counting experiments were performed with both DC and pulsed injection, showing in both cases clear suppression of the multi-photon probability.

Due to their small dimensions and their discrete density of states, quantum dots can be expected to show long charge carrier spin flip times. The main reason for this is that the dominant elastic and inelastic spin-flip mechanisms involve energy changes less than the spacing between the discrete levels of the dot, and are therefore largely forbidden. Investigations into the charge carrier spin dynamics include a study by Bacher \textit{et al.}\textsuperscript{18}, who measured the emission lifetimes of the exciton and the biexciton in an isolated CdSe quantum dot. They showed how a simple rate-equation model can be applied to analyze the dynamics, and extracted a spin flip time for the exciton much longer than the exciton radiative lifetime.

A more detailed study of the spin dynamics of excitons in self-assembled InAs/GaAs quantum dots was reported by Paillard and co-workers\textsuperscript{18}. Excitons were excited in the dots by resonant optical excitation, allowing direct interrogation of the spin-flip mechanisms in the dots, without bulk processes occurring during carrier capture. The polarization of the dot emission line, under polarized excitation, was measured and found to remain constant during the emission lifetime of the dot exciton, for temperatures up to 30 K.
Another important result of this work was the finding that under linearly polarized pump light, the quantum dot emission was linearly polarized. A naïve assumption would be that the emission should be unpolarized, and indeed it can only be linear if the normal selection rules for the optical transition break down. This can occur, however, in the case of quantum dots of reduced symmetry. The anisotropic exchange interaction, resulting, for example, from the elongation of the dots along the [110] crystallographic direction, results in the superposition of the circularly polarized transitions, |±1⟩, to give 2 linearly polarized lines: 

\[ |x⟩ = \frac{|+1⟩ + |−1⟩}{\sqrt{2}} \quad \text{and} \quad |y⟩ = \frac{|+1⟩ − |−1⟩}{i\sqrt{2}}. \]

The anisotropic exchange splitting poses a significant problem for the generation of entangled photon pairs using the bi-exciton cascade. To understand why this is, we should first consider the nature of the desired 2 photon entanglement. A quantum dot populated by two excitons in their ground states is analogous to an atom with two electrons. Due to the Pauli exclusion principle, the electrons in the atom must possess opposite angular momenta. The same holds for the excitons in a quantum dot, with the difference that since there are two particles present, the spins are not ±\(\frac{1}{2}\), but ±1, giving rise to the |±1⟩ labeling for the states introduced above. Due to this integer spin, the selection rules permit the co-annihilation of the electron and the hole, which is of course accompanied by the emission of a photon of the appropriate helicity. Furthermore, both the |+1⟩ and |−1⟩ states that may be left behind following the recombination of the first exciton are degenerate. The possibility for entanglement to arise during the recombination of the two excitons in a dot is a result of the necessarily opposite helicity of the two sequentially emitted photons. Thus measuring the polarization of any one of them gives complete information about the polarization of the other photon, in the same basis. It is perhaps one of the most puzzling facts in modern physics, however, that this entanglement relies upon the polarization of each photon being not determined at the moment of emission, but remaining indeterminate until the moment of detection.
Where there is an anisotropic exchange interaction present, however, the mixing of the two circular polarization states to produce two linearly polarized states is accompanied by a splitting of the degeneracy of the single-exciton states, meaning that in principle the polarization of the photon emitted by the single exciton can be inferred from the photon’s energy, and the polarization states of the paired photons are no longer indeterminate at the moment of emission. Thus, the desired quantum mechanical entanglement is destroyed and replaced by a classical polarization correlation, which can be made to disappear upon rotation of the linear polarization basis used for detection.

A method to recover the entanglement of the photon pairs emitted by an InAs/GaAs dot was developed by Stevenson et al.\textsuperscript{20}, who used polarization sensitive spectroscopy to identify dots with small enough exchange splittings that the degeneracy of the two ground-state levels could be re-established by the application of an in-plane magnetic field. With the states made to overlap energetically it was possible to observe polarization correlations that were independent of the angle of the detection basis, thus demonstrating entanglement.

As mentioned above, one of the advantages of using semiconductor quantum dots, inside a solid semiconductor material, is that the single-photon emitter can be placed inside a larger heterostructure, capable of confining the light emitted by the dot. In such structures, the ‘hetero’ materials can be different semiconductors, air, or air spaces infiltrated with other materials. A common form for such microcavities is the so-called micro pillar, which consists of an etched column of semiconductor, about 1 µm in diameter. The dot is positioned inside this pillar, between two multi-layered Bragg reflectors. The narrow lateral dimension of the pillar and associated refractive index contrast provides lateral optical confinement, while Bragg mirrors above and below the dot can produce strong enhancement of the light emission in the vertical direction. One of the main advantages of this scheme for a single-photon source is that the photon collection efficiency from the dot can be hugely improved. Due to the Purcell enhancement, there can also be effects of enhancement of the emission rate and
suppression of any nonresonant emission. The first case of single-photon emission from a quantum dot inside a micro pillar was reported by Moreau et al.\textsuperscript{21}.

While the main objective of producing single quantum dots inside micro cavities is to affect control of the optical emission, carrier confinement is also a possibility. Inspired, presumably, by the problem of the surface roughness of an etched micro pillar, Ellis et al.\textsuperscript{22}, designed and implemented another type of microcavity. In this case, lateral confinement was provided not by etched side walls, but by a thick apertured layer of aluminium oxide, grown above the dot. The oxide aperture was narrow enough to allow electrical carrier injection selectively into one dot, while the index contrast between the oxide and the aperture offered the desired confinement of the optical mode.

1.3 Overview of the rest of this thesis

This thesis describes empirical studies of the basic optical properties of individual InAs/GaAs quantum dots, focusing mainly on the spontaneous emission lifetimes, anomalous PL decay kinetics at high pump powers, and the longitudinal spin flip processes in isolated dots. The principal technique employed in these studies is time-correlated single photon counting.

A single sample of self-assembled InGaAs/GaAs was employed throughout the sequence of measurements described. The quantum dots studied were grown at high temperature, resulting in a low density of wide but low circular dots, with substantial incorporation of Ga into the dots from the surrounding material. This latter leads to short-wavelength emission from the dots, between 900 and 1000 nm. Some of the consequences of these properties will emerge as the experimental results are discussed.
Chapter 2 describes the experimental system, including some of the details of the sample growth, and resulting general properties of the dots. The equipment and methods used to achieve low-temperature micro PL are discussed in detail. The principles and implementation of the time-correlated single photon counting technique, used for photon correlation experiments, PL lifetime measurements, and analysis of spin dynamics, are detailed, including a description of the data processing algorithms employed.

Chapter 3 details a series of measurements of quantum dot exciton emission lifetimes, over the full range of the sample emission envelope. The exciton emission time is shown to exhibit a strong increase with increasing emission wavelength. Correlating this observation with measurements of the in-plane diamagnetic shift leads to the conclusion that the energetic position of a dot within the emission envelope is governed by the dot’s height, rather than the width of the dot as is often assumed. It is thus found that the emission lifetime depends primarily on the height of the dot. These facts provide evidence that for these mesoscopic dots, the exciton oscillator strengths are more reminiscent of a thin quantum well.

In chapter 4 is reported the discovery that at high pump powers, above the saturation point of the exciton, the PL transience from an isolated dot can exhibit non-monotonic decay, consisting of two distinct peaks. For these double-peaked transients, the time-resolved PL is found to be composed of an initial peak from some sample background emission, and a delayed peak from the quantum-dot exciton. Several models of this behaviour are investigated, including multi-excitonic cascaded PL decay, and a model termed the ‘game-over scenario,’ in which the background emission and the sharply peaked exciton PL are treated as originating from the same quantum dot transition, in different ambient charge environments. We propose an alternative explanation, in which high densities of charges external to the dot screen the exciton binding, leading to the observation of the sharply peaked exciton PL only after the external carriers have recombined.
Chapter 5 describes time-resolved measurements of the dot PL polarization, under the condition of a circularly polarized pump. These measurements permit investigation of the exciton longitudinal spin flip processes. The PL polarization following a short laser pulse is found to undergo an initial decay, after which it rises again to values up to 50%. Spectroscopic studies show that the individual quantum dot exciton lines exhibit weak Overhauser shifts of about 5 $\mu$eV, proving that the nuclei in the dot are optically orientated by the polarized pump. It is the interaction of the excitons with these optically aligned nuclear magnetic moments that is interpreted as the cause of the rising PL transience. Measurements of Overhauser shifts have been used several times in the literature on quantum dots to provide a register of the degree of nuclear polarization, but in cases where the electron g-factor has not been separately determined, such measurements of the nuclear spin orientation are vulnerable to inaccuracy. By introducing a simple rate-equation model, we demonstrate that measurements of the polarization transience give a good indication of the degree of nuclear alignment. This in turn permits, in principle, an estimate of the electron g-factor.
Chapter 2:

Experimental Methodology and Sample Details

2.1 Sample

A single layer of self-assembled InGaAs quantum dots was grown by molecular beam epitaxy on an undoped GaAs [100] substrate. InAs was deposited onto the GaAs to a depth of 0.6 nm (2 mono layers), at a temperature of 530°C, followed by a 15 second growth interrupt before growth of the GaAs capping layer. The effects of the relatively high growth temperature are a low density of rather large quantum dots and an intermixing of Ga into the quantum dot layer. This Ga intermixing leads to rather shallow confinement, meaning that there is less difference between exciton energies inside and outside the dot, compared to pure InAs dots, and consequently shorter emission wavelengths from the dots. The dot density was estimated from atomic-force microscope (AFM) measurements on a second layer of nominally identically grown quantum dots positioned on the top of the sample, giving about $4 \times 10^9$ dots per cm$^2$. The AFM images also revealed the heights of the dots to be $4.1 \pm 0.9$ nm, and the base to be predominantly circular in shape, with a diameter of $72 \pm 9$ nm, where ‘±’ indicates the standard deviation of the distribution. The heights of the capped dots, used for spectroscopy, may be slightly different from those of the uncapped dots characterized by the AFM investigation. Figure 2.1 shows a representative AFM scan of a $2 \times 2$ µm area of the sample surface, provided by T. Mano. According to the nomenclature of the growers, this sample has been dubbed ‘R80’.
Figure 2.1: Atomic-force microscope image of the sample surface, showing a 2 x 2 µm area populated by quantum dots grown under nominally identical conditions as those producing the luminescence, and on the surface of the same wafer. Image recorded by T. Mano.

Figure 2.2: Macro-photoluminescence from the sample at a temperature of 4.1 K. The emission consists of three main features: (A) ground-state emission from the quantum dot excitons, (B) a band of discrete emission lines, probably due to small thickness fluctuations in the wetting layer, and (C) the wetting layer emission.
An estimate of the effect of the non-zero AFM tip width on the measured size of the quantum dots was performed. The measured feature profile can easily be seen to be the convolution of the actual feature with the AFM tip profile. Smaller dots on another sample, measured with the same AFM tip, exhibited sizes down to 7 nm. Since the convoluted feature size is always greater than the tip size, we can be certain that the tip is not more than 7 nm wide. We can take, therefore, 7 nm as an over-estimated tip size and 70 nm as the broadened dot size. Approximating the tip and dot profiles as Gaussian, we can apply the rule that the convoluted width is equal to the square root of the sum of the squares of the tip width and the true dot size, i.e., the true dot size is $\sqrt{70^2 - 7^2}$ nm, which is only very slightly lower than the measured 70 nm. There is thus good justification for ignoring convolution effects on the measured feature sizes.

The luminescence from the quantum dot ensemble is peaked at about 955 nm (1.3 eV), with a full width at half maximum of about 50 nm (68 meV). Figure 2.2 shows the ensemble luminescence. Three broad features appear on the macro-PL spectrum: the quantum dot exciton emission (centered at 955 nm), a sharp band of discrete emission lines at 870 nm, and the wetting-layer emission, peaked at 850 nm.

The feature at 870 nm breaks up into a series of very sharp emission lines in micro-PL, and is most likely due to fluctuations in the thickness of the wetting layer, causing weak three-dimensional confinement. This 870 nm luminescence band shows strong temperature dependence, being totally eliminated at 40 K, while the Stranski-Krastanov dots (feature ‘A’) continue to emit strong luminescence at 140 K. At high pump powers, in micro-PL, a series of emission lines appears between features ‘A’ and ‘B,’ which are assumed to originate from the first excited states of the Stranski-Krastanov dots. The asymmetry of the QD emission envelope, as seen in Figure 2.2 has been shown in power- and temperature-dependent PL experiments to be not due to excited-state recombination $^{24}$. 
2.2 Photoluminescence studies of individual quantum dots

The samples were placed in a helium flow cryostat, manufactured by Cryovac. Stable operation of this cryostat is possible at virtually all temperatures from room temperature down to 4.1 K. A small amount of a zinc-based paste was applied to the cold finger of the cryostat before mounting the sample, to provide a good thermal contact. When necessary, to verify that a good enough thermal contact was achieved that the sample temperature matched closely the temperature of the thermocouple inside the cold finger, the temperature dependence of emission lines of known wavelength, such as the GaAs bulk exciton, was examined.

Excitation laser light was brought onto a beam splitter, from where it was reflected through 90° into a ×100 objective lens with a large numerical aperture of 0.75. Using this objective lens, the pump light was brought into focus on the sample surface, with a small enough spot size ($\approx 1 \, \mu m$) to excite a relatively small number of quantum dots. The excitation wavelength used in most experiments was about 765 nm, corresponding to a photon energy above the GaAs bandgap. Electron-hole pairs excited in the bulk material by the pump laser then relaxed into nearby quantum dots, and subsequently recombined, giving rise to a photoluminescence signal. A sliding power meter was installed on a rail, allowing it to be easily inserted directly above the objective lens in order to monitor the pump power.

The emitted photoluminescence was collected by the same objective lens used for excitation, and passed to the same beam splitter used to direct the excitation light into the objective lens, from which it was transmitted towards either one or two monochromators, depending on the nature of the experiment. For the experiments in Chapters 3 and 4, the beam splitter took the form of a ‘hot-cold’ mirror, exhibiting the property that light of wavelengths corresponding to the sample photoluminescence is preferentially transmitted, rather than reflected, in order to maximize the amount of luminescence.
available for detection. For the polarized PL measurements described in Chapter 5, the ‘hot-cold’ mirror was replaced by a polarization-preserving cube beam splitter.

A 40 mm lens focused the collected optical signal onto the entrance slit of a 50 cm monochromator, supplied by Acton Research Corporation, to spectrally analyze the sample photoluminescence. The rotatable turret inside the monochromator gave a choice of three possible gratings, with 300, 600, or 1200 grooves per mm. The gratings all had blazing angles optimized for a wavelength of 1 µm. A movable mirror in the monochromator gave a choice of two exit windows. The first led to a silicon charge-coupled device (CCD) detector, produced by Princeton Instruments. This CCD offered a broad detection window, with a resolution, in conjunction with the 1200 groves/mm grating, of about 170 µeV at the relevant wavelengths. The other exit port consisted of a narrow slit, followed by a focusing system used to couple the spectrally filtered emission into an optic fibre with a core diameter of 100 µm. This fibre then transmitted the signal to a single photon counting module, produced by Perkin Elmer, consisting of a silicon avalanche photodiode (APD) operated in Geiger mode. This APD exhibits a dark count rate of about 30 photons per second. With entrance and exit slit both fixed at 50 µm, which was wide enough not to reduce significantly the intensity of a sharp emission line from a single dot, a spectral resolution of 80 µeV was normal. These APDs formed the basis of the time-correlated single photon counting technique, described later. Scanning of the monochromator grating and registration of the counts detected by the APD was performed using a customized LabVIEW interface.

In addition to the spectral resolution, another important property of the spectroscopic setup is the repeatability of the position of a narrow emission peak. This was measured by repeatedly scanning the monochromator grating over an emission line from a Xe calibration lamp. The line used was the 916 nm line, and the intensity was recorded using one of the APDs. Sixteen scans were performed, and the peak position was obtained for each scan using a built-in peak-finder routine in LabVIEW. The standard deviation for the fitted peak position was 1.96 µeV. This variation, however,
also included a significant systematic drift over the course of the measurements, almost certainly due to slow variation of the temperature of the Xe gas inside the calibration lamp.

To facilitate the optimization of the photoluminescence from a single quantum dot, the cryostat was equipped with a three-dimensional micro-positioning stage, produced by Micos. The positioning stage had a nominal minimal step of 1.5 nm. Focusing and x-y optimization of sharp emission lines could be achieved either coarsely, with a joystick, or more carefully using the same LabVIEW interface used to communicate with the monochromators and APDs.

Because the quantum dot density of the sample made the isolation of individual emission lines difficult, three techniques were investigated to allow single-dot spectroscopy: aluminium masking, etched mesas, and solid immersion lenses. One small piece of the wafer was prepared with an array of etched mesas of various sizes up to 1 µm across, but the damage inflicted during the etching process reduced severely the photoluminescence efficiency. Other samples were prepared with opaque aluminium masks deposited on top. The masks included arrays of square apertures defined by electron beam lithography, allowing luminescence to be excited and collected. Masks with 1 µm apertures were quite successful in terms of isolation of single emission lines, and gave reasonable detection efficiency, but were not as successful as the third technique investigated.

The best approach for single dot spectroscopy found during this research was to mount a solid immersion lens (SIL) on the sample surface. These are glass beads, about 1 mm in diameter, and shaped as a truncated sphere. A tiny amount of vacuum grease was applied as a glue between the sample surface and the flat side of the SIL. The effects of the SIL are to reduce the size of the focused laser spot on the sample from 1 µm to as little as 400 nm and, by frustrating the total internal refraction at the sample to air interface, to increase the amount of photoluminescence collected by the objective lens. Supposing that only the dots located inside this 400 nm spot are excited by the laser, then
from the dot density stated earlier, we can expect to see luminescence from approximately 20 dots at any given location.

To estimate the impact of the SIL on the photon collection efficiency, we note that for a hemispherical SIL, the effective numerical aperture of the system becomes \( NA_{\text{obj}} \times n_{\text{SIL}} \), where \( NA_{\text{obj}} \) is the numerical aperture of the microscope objective and \( n_{\text{SIL}} \) is the refractive index of the SIL, which is 1.83. This yields \( NA_{\text{eff}} = 1.37 \). The collection efficiency can be approximated as

\[
\eta = \frac{1}{32} \left[ 15 - \left( 1 - \frac{NA}{n_{\text{semi}}} \right)^2 \right] + \left( 1 - \cos \left( 3 \arcsin \left( \frac{NA}{n_{\text{semi}}} \right) \right) \right),
\]

where \( n_{\text{semi}} \) is the refractive index of the GaAs semiconductor, which is 3.5. This formula yields efficiencies of 1.72 \%, without any SIL and 5.77 \% with the SIL. While the achieved efficiencies during this work were always much less than these predictions, the ratio for the cases with and without SIL matches well with the general experience.

Nearly all the photoluminescence experiments described in this thesis made use of a SIL. The main disadvantage of the SIL, compared to an Al mask is that with a mask, the same aperture can be investigated day after day, while with the SIL it is not possible without great luck to locate the same quantum dot twice.

The pump laser used in nearly all experiments was a Ti:sapphire tunable and mode-lockable Mira 900 laser supplied by Coherent. The output wavelength for all reported experiments was 765 nm. In pulsed operation, pulses of a few picoseconds in duration were produced with a frequency of 76 MHz, corresponding to a pulse period of 13 ns.
2.3 Time-correlated single photon counting

All time-resolved measurements presented in this thesis employed the time-correlated single photon counting method. To perform this technique, a TimeHarp 200 time-correlator card produced by PicoQuant was utilized. This device serves to time the separation between two input pulses at different ports on the device to picosecond resolution, then provides on-board histogramming to obtain the number of coincidences as a function of the time delay between the two signals.

The two ports on the time-correlator are termed the Start and the Sync. The Start signal is always taken from the output of one of the APD single-photon detectors, and therefore corresponds to either a detector dark count or, much more often, the registration of a photon emitted by the sample. This signal starts a digital clock with picosecond resolution which runs either until the device times out or until a pulse is received at the Sync port. The Sync signal serves as a time reference and stops the clock. The time between the two signals constitutes the data added to the histogram that provides the time-resolved information from the experiment. A multiplexer, also produced by PicoQuant, installed before the Start input allowed up to four signals to be processed in parallel, and was sufficient to record PL simultaneously from the two APDs, attached to the two monochromators used in the experiments.

Three options were used for the Sync source, and were interchangeable using an electronic switch, again controlled by the LabVIEW interface. The first option was a function generator providing sharp pulses at a rate of 200 kHz. This option was employed when time-resolved information was not desired, and simply provided a means for the computer to record the PL counts registered by the single-photon detectors. The high-resolution PL scans of isolated quantum dots were performed by this means.

The second option for the Sync source was to use the second APD. With one APD attached to the Start and the other attached to the Sync, it was possible to analyze the
photon statistics for the emitted PL, such as measuring the autocorrelation function, as will be described shortly, in Section 2.5.

![Diagram of experimental arrangement](image)

**Figure 2.3:** Schematic of the experimental arrangement for the exciton lifetime measurements. The device marked ‘APD’ is the avalanche photodiode.

The third possibility for the Sync source was to use the output of a fast photodiode, known as the trigger diode, exposed to a beam split off from the pulsed laser used to excite the PL. This, in essence, is probably the most common application of the time-correlated single-photon counting technique, and dominates this thesis, being the major topic of Chapters 3, 4, and 5. In this configuration, depicted schematically in Figure 2.3, the histogram of coincidences between the laser and the PL, plotted against time, contains the PL build-up and decay times. An additional requirement, though, is that the photon flux at the detector used to monitor the PL is much less than one per laser pulse. Failure to comply with this condition results in a phenomenon known as ‘pile-up,’ whereby the
apparent lifetime of the charge excitations in the sample is less than the real lifetime, due to the high probability of receiving more than one pulse at the Start input before each Sync pulse: all photons arriving after the first can not be recorded.

An intuitive ordering of the signals for this third, and generally most important, implementation of the time correlator would be to have the voltage pulse from the laser arrive first, and then to time the period between the laser pulse arriving and the PL photon being emitted. This, however, introduces an unnecessary computational overhead, as most of the occasions when the Start is triggered, there will be no accompanying PL photon. This is why the Start input is received from the sample, rather than from the reference, a technique known as ‘reverse start-stop mode.’ Since the laser pulses appear periodically, it makes no difference to the time-resolved information, except that the PL decay curve is reversed, a matter that is automatically corrected with subsequent processing.

It should be clear that the exact timing between the Start and Sync pulses is quite irrelevant in these experiments, as there is no definitive zero time delay. For the lifetime measurements, therefore, some tinkering with optical path lengths and electronic cable delays was usual in order to the position the start of the time-resolved PL signal conveniently at the beginning of the available measurement window.

The TimeHarp 200 correlator card has a range of user-selectable time resolutions, from 1 ns down to 37.5 ps. This maximum resolution of 37.5 ps was confirmed experimentally by sending the output of a single APD to both the Start and Sync inputs. The histogram in this case consisted of a single spike, of width equal to one histogram bin, confirming that simultaneous events never appear separated by more than the minimum bin width. The 37.5 ps resolution was selected for all the lifetime measurements described in this thesis.

Despite this very small timing uncertainty in the electronics, much larger timing jitter was present in the actual experiments. This jitter, referred to as the instrument response function (IRF), is due to other components in the setup, such as the width and
jitter of the laser pulses and the detectors used for the Start and Sync signals. The laser produces very narrow (3.5 ps) pulses with a highly reproducible period and contributes almost nothing to the IRF. The dominant component of the IRF was found to be the APDs, with the result that IRFs of 650 and 1100 ps were recorded for Sync signals provided by the trigger diode and the second APD, respectively. This broad timing uncertainty of the APDs is due to their being optimized for high detection efficiency, which is achieved using a wide absorption region. Other detector designs using a narrow absorption region inside an optical cavity may be able to provide much smaller timing uncertainties, without reducing the fraction of photons absorbed, though no such design was commercialized when our APDs were purchased.

The standard practice when performing time-resolved measurements was to measure also an IRF by tuning the monochromator grating to the laser wavelength and accumulating a histogram in the same manner as the experiment just performed. This empirical IRF was indispensable when subsequently analyzing the data, as it allowed the true time-dependence to be extracted from the experimental histogram, despite the broad timing uncertainty of the setup.

2.4 Data analysis: Fitting the PL lifetime measurements

With the Sync port of the TimeHarp correlator card connected to the voltage output of the trigger diode illuminated by the pulsed excitation laser, the histogram of coincidences vs time delay, $\Delta t$, is proportional to the probability that an isolated quantum dot under investigation is occupied by an exciton. Two things are required in order to analyze such data sets: (i) a model of the PL dynamics and (ii) knowledge of the timing uncertainty of the experimental setup, known as the IRF.
It is readily seen that the time-dependent signal measured by the time-correlated photon counting method is a convolution of the real transient phenomenon with the IRF. In principle, therefore, deconvolution of each measurement with this IRF should yield the desired dynamics. In practice, however, deconvolution of real, noisy data is an unpredictable computational procedure. Instead, a process known as reconvolution is the standard practice\cite{27}.

Reconvolution employs a model function with a set of variable parameters, which is convoluted with the IRF, the result of which procedure is compared with the measured data. Finding the best fit then consists of adjusting parameters so as to optimize some statistic derived from this comparison. As with many cases, the maximum likelihood estimate for the correct model parameters for the PL lifetime measurements is obtained by minimizing $\chi^2$.

In order to define a model with which to fit the PL transients for single-excitons, we can start from a system of two rate equations:

$$\frac{dB}{dt} = -\frac{B}{\tau_c}$$

$$\frac{dX}{dt} = \frac{B}{\tau_c} - \frac{X}{\tau_r}$$

where $B$ and $X$ are the exciton populations in the barrier and in the dot, respectively, and $\tau_c$ is the capture time for the quantum dot, which includes the time required for the exciton to relax to the quantum dot ‘ground state,’ and $\tau_r$ is the exciton recombination time. The exact solution for $X(t)$, with $B(0) = 1$ and $X(0) = 0$ is

$$X(t) = \left( \frac{e^{\frac{-t}{\tau_c}} - e^{\frac{-t}{\tau_r}}}{\tau_c - \tau_r} \right) \tau_r.$$
Making the assumption $\tau_c \ll \tau_r$ yields an approximate solution, given by Equation 2.1, which was successfully applied to all the low-power lifetime measurements performed, including those detailed in Chapter 3.

$$I(t) = (1 - e^{-t/\tau_c}) \times e^{-t/\tau_r} \quad \text{(Equation 2.1)}$$

Here, $I(t)$ is the time dependent PL intensity. In order to generate a curve for comparison with the data set, three additional parameters were required: (i) a shift, needed to move the model curve laterally on the time axis, (ii) an offset, required to account for the constant level of dark counts, and (iii) a parameter to rescale the curve following convolution. An example of one of the lifetime measurements performed and its associated fitted model curve are presented in Figure 2.4. While only 29 points are plotted on the model curve in Figure 2.4, the actual fit used 270 points, one for each point in the data.

As most data-analysis packages do not allow fitting functions that incorporate the convolution step to be defined, a custom procedure was written in Matlab to perform the fitting and extract the desired time constants. The Gauss-Newton method was implemented to perform the optimization. This algorithm consists of no more than iteratively solving the normal equations,

$$\left(J_r^T J_r\right)\Delta = -J_r^T r,$$

where $\Delta$ is the desired vector used to increment the model parameters, $r$ is the vector of residuals, $J_r$ is the Jacobian matrix of $r$ with respect to the vector of model parameters, and superscript ‘T’ represents the matrix transpose operation. The procedure was iterated until the fit was deemed to have converged, as judged by the failure to improve substantially the Pearson correlation coefficient, $R$, compared to the previous iteration.
Figure 2.4: Low pump-power lifetime measurement performed on an isolated quantum dot exciton emitting at 928 nm at 4.1 K. The continuous curve shows the data, accumulated over 10 minutes. The hollow circles show a sample of the fitted model curve, using equation 2.1. The squared correlation coefficient for the fit, $R^2$, is shown, along with the fitted rise and decay times. The peak of the data curve is about 10,000 counts, and the entire measurement consists of about half a million registered photons.

Starting from a reasonable initial guess for the model parameters, obtained by visual inspection, this method usually converged quickly (less than 10 iterations) and robustly (slight adjustment to the initial guess did not affect the end result) to a solution with a squared correlation coefficient, $R^2$, usually greater than 0.999, which is indicative of an almost flawless fit.

The error bars provided for the quantum dot exciton lifetimes presented in Chapter 3 were obtained empirically, by repeated measurement of a single isolated dot. This procedure is valid as the signal-to-noise ratios for all the measurements are very similar. Lifetime measurements were performed ten times on a particular quantum dot emission line, and the standard deviation of the fitted lifetimes was about 40 ps. Thus, it is verified that using the reconvolution procedure, the statistical error in the
measurements is reduced from the experimental timing uncertainty to approximately the resolution of the time correlator card.

2.5 Autocorrelation experiments on isolated quantum dots

In the introductory chapter, it was explained that an individual quantum dot can serve as a source of single photons, and that single-photon emission can be demonstrated by performing autocorrelation experiments. Time-correlated single photon counting forms the basis of such measurements. Such experiments were performed during this research project, and the related cross-correlation experiment constituted an important tool in the investigation of the high-pump-power luminescence from quantum dots, presented in Chapter 4. The setup used to perform these experiments is shown schematically in Figure 2.5.

Using a 50%/50% beam splitter, the sample PL was divided equally and directed to the entrances of two monochromators and, further onto the two APDs. If the two monochromators are set to the same wavelength, and the outputs of the two APD are sent respectively to the Start and Sync inputs of the time correlator, then the histogram of coincidences vs time delay, Δt, is proportional to the second-order correlation function, $g^{(2)}(Δt)$, for the emission source

$$g^{(2)}(Δt) = \frac{\langle I(t)I(t+Δt)\rangle}{\langle I(t)\rangle^2},$$

where $I(t)$ is the intensity emitted at time t. For a single photon emitter, this function looks like the lower curve in Figure 1.1, except that $g^{(2)}(Δt)$ should be equal to 1 at time delays far from $Δt = 0$, and the suppression at $Δt = 0$ is complete for an ideal single-photon emitter.
In order to record events with both positive and negative time delays, a delay cable a few meters in length was added before the Sync input. This allowed the recording of coincidences where the Sync photon arrived at its detector before the Start photon arrived at its detector, even though the correlator card is not triggered until a signal arrives at the Start input.

![Diagram](image)

Figure 2.5: Experimental arrangement for performing autocorrelation and cross-correlation experiments.

The path lengths to the two monochromators were arranged to be as close to equal as possible, with a difference of less than 5 mm between them, corresponding to a difference in time of flight of less than 16 ps, which is less than the minimum bin width for the time correlator. This made it easy to determine the new position of the zero time delay, after the delay cable was inserted. A ‘T’-shaped divider was added to the output of one of the APDs, and the cables used for both the Start and Sync signals were connected.
to it. A short histogram recorded in this configuration consisted of all coincidence appearing in a single histogram bin, at the position of $\Delta t = 0$.

As indicated, $g^{(2)}(0)$ for an ideal single emitter is equal to zero. For two identical single emitters, $g^{(2)}(0) = 0.5$. This implies that a correlation function suppressed at $\Delta t = 0$ to less than 0.5 constitutes very strong evidence of single-photon emission from a quantum dot.

The expected values for $g^{(2)}(0)$ with different numbers of particles can be established by considering the general case of $n$ identical single-photon emitters. The two detectors are labeled A and B, and the count rates of the detectors are labeled $N_A$ and $N_B$. There is assumed to be no background signal or noise of any kind present, and the IRF is assumed to be a delta function. The correlation at $\Delta t = 0$ is composed of $n \times (n-1) \times \frac{1}{2}$ cross-correlation terms. The coincidences for each emitter with itself vanish at $\Delta t = 0$.

Considering one such term, that due to coincidences between emitter 1 and emitter 2, the probability to get a photon from emitter 1 onto detector A during the time equal to the correlator time bin, $t_b$, is:

$$P(1, A) = \frac{1}{n} N_A t_b$$

and the probability to get a photon from emitter 2 onto detector B in the same period is

$$P(2, B) = \frac{1}{n} N_B t_b.$$ 

Accounting for the possibility to also have A triggered by source 2, etc., the number of coincidences during an accumulation of duration $t_{\text{accum}}$, due to these two sources is twice the product of the two terms above:

$$\text{Coincidences}_{1,2} = \frac{2}{n^2} N_A N_B t_b^2 \frac{t_{\text{accum}}}{t_b}.$$

To normalize these coincidences to we must divide by $N_A N_B t_b t_{\text{accum}}$, giving
And since there are \( n \times (n-1) \times \frac{1}{2} \) terms in total, then the correlation function at \( \Delta t = 0 \) is

\[
g^{(2)}(0) = \left(1 - \frac{1}{n}\right).
\]

An emission line from a quantum dot, giving approximately 10,000 photo-counts per second, was located at 914 nm, and subjected to an autocorrelation measurement. The PL was scanned with both monochromators, providing the data in Figure 2.6. These scans were performed using a time resolution of 0.3 ns, which is why the count rates are less than 2500. This is the same time resolution as was used for the autocorrelation, and represents a compromise between maximizing the number of data points over the expected antibunching dip, and not lowering the coincidence rate too much. Lower time resolution results in a higher count rate, and since the coincidence rate is determined by the product of the count rates on the two detectors, several hours can be needed to accumulate a good histogram.

The autocorrelation data in Figure 2.7 were recorded over two and a half hours, with the pump laser operated in continuous-wave mode. The figure shows the normalized histogram of coincidences, obtained by simply dividing the entire histogram by the average signal at \( |\Delta t| \gg 0 \). Also shown are the results of a fitting procedure, used to investigate the effects of the system timing uncertainty on the depth of the antibunching dip.
Figure 2.6: Scans of the PL of an isolated quantum dot on both monochromators. The strong emission line at 914 nm was used for the antibunching experiment shown in Figure 2.7.

Figure 2.7: Autocorrelation function measured for a QD emission line at 914 nm (green). A time resolution of 0.3 ns was used for the measurement. A fitted model function before (red) and after (blue) convolution with the measured IRF are also shown.
The IRF was measured by autocorrelating the pulsed laser, and was found to be well approximated by a Gaussian curve, with full width at half maximum equal to 1.036 ns. The model function used for the fitting was:

\[
g^{(2)}(\Delta t) = 1 - ae^{\frac{-|\Delta t - h|}{\tau}},
\]

where \(a\) determines the depth of the antibunching minimum, \(h\) implements a fine tuning of the position of \(\Delta t = 0\), and \(\tau\) is the time constant determining the temporal width of the antibunching dip. This time constant should be approximately equal to the quantum dot recombination time, but also incorporates the dot capture time.

The above trial function was convoluted with the fitted IRF, and optimized, as with the lifetime measurements, using the method of least squares. The fitted antibunching minimum, \(a\), was 0.9, and \(\tau\) was determined to be 0.75 ns, which agrees well with the lifetimes expected at this wavelength, based on the data presented in Chapter 3.

The obtained value for \(g^{(2)}(0)\) clearly constitutes a demonstration that the studied quantum dot emits photons only one at a time. The suppression of \(g^{(2)}(0)\) is not complete, however, and the remaining 10% coincidence rate (after extracting the effect of the IRF) still needs to be accounted for. From the spectral scans, an estimated signal-to-background ratio of 11.7 was determined. This background signal results in part from the detector dark counts, but the much more significant contribution comes from the sample itself. The effect of such a background can be analyzed by considering the background photons to be completely uncorrelated.

The measured correlation function, \(g^{(2)}_{\text{m}}(\Delta t)\), can be seen to be composed of three terms:

(a) coincidences between photons from the single emitter
(b) coincidences between single-emitter photons and background photons
(c) coincidence between background photons
We can assume that \( N_A = N_B = S + B \), where \( S \) is the number of detected photon from the single emitter and \( B \) is the corresponding number from the sample background. Then, to obtain term (a), observe that the normalized number of coincidences between photons from the single emitter at time delays much larger or smaller than zero will be 
\[
\frac{S^2}{(S + B)^2}.
\]
To see how the normalized coincidences vary at time delays close to zero, we can multiply the above term by the ideal correlation function for the dot, \( g^{(2)}_{QD}(\Delta t) \).

Term (b) is arrived at by summing the 2 ways that background photons can coincide with photons from the single emitter, and again normalizing, giving 
\[
\frac{2SB}{(S + B)^2}.
\]

The final term follows easily from a similar argument, and can be combined with the other terms, giving:

\[
g^{(2)}_m(\Delta t) = \frac{g^{(2)}_{QD}(\Delta t) \times S^2}{(S + B)^2} + \frac{2SB}{(S + B)^2} + \frac{B^2}{(S + B)^2}
\]

The last two terms can be seen to be equal to \( 1 - \frac{S^2}{(S + B)^2} \), giving

\[
g^{(2)}_m(\Delta t) = \frac{g^{(2)}_{QD}(\Delta t) \times S^2}{(S + B)^2} + \frac{S^2}{(S + B)^2}
\]

This can be simplified by substituting \( \rho = \frac{S}{S + B} \). Proceeding to solve for \( g^{(2)}_{QD} \) to determine what the ideal autocorrelation function for the dot would look like, if there was no background signal present produces:

\[
g^{(2)}_{QD}(\Delta t) = \frac{g^{(2)}_m(\Delta t) - \left(1 - \rho^2\right)}{\rho^2}
\]

Using the above formula, and the observed signal-to-background ratio, the autocorrelation function for the dot alone at \( \Delta t = 0 \) can be determined to be not significantly different from zero.
Results such as this example of photon antibunching observed in the emission from an isolated quantum dot constitute the most definitive evidence we have for the quantization of the electromagnetic field. The fact that the energy conveyed by a single photon does not divide into separate detectable streams at a beam splitter is demonstrated by the suppression of the second-order correlation function at $\Delta t = 0$, and clearly establishes the particular nature of light. It is perhaps as amusing as it is puzzling to reflect that in order to achieve this demonstration, we have utilized in the monochromator interference effects that rely completely on the wave nature of light.

A sharp emission line at 876 nm, in the feature labeled ‘B’ in Figure 2.2, was also subjected to an autocorrelation experiment, and again revealed the clear antibunching signature of a single-photon emitter. This confirms the suspicion that these emission lines are also due to charge carriers subjected to quantum confinement in three dimensions. This adds weight to the interpretation that they are the result of nano-scaled confinement in thickness fluctuations of the wetting-layer quantum well, similar to previously reported observations$^{29}$. 
Chapter 3:

The role of dot height in determining exciton lifetimes in shallow InAs/GaAs quantum dots

Abstract:

The spectral dependence of the recombination lifetime has been measured for individual self-assembled InGaAs/GaAs quantum dots, over the entire emission envelope, by time-resolved micro-photoluminescence experiments. The measurements show a rising trend with increasing emission wavelength, increasing from 680 ps at 900 nm to about 1020 ps at 990 nm. Measurements of the out-of-plane diamagnetic coefficients for the dots show almost no correlation with wavelength. The observed trend in the lifetimes is interpreted in terms of the emission energy being predominantly determined by the dot height.
3.1 Introduction

The great scientific interest in quantum dots arises from two features, (i) they offer the opportunity to perform fundamental experiments on artificial atoms with a range of properties unavailable with real atoms, and (ii) they show considerable potential for application in functional devices, in areas such as light emission and quantum information processing. In optoelectronic applications, the emission time constant of a quantum dot is vital as it plays a large part in determining the device efficiency and, in some cases, the repetition rate. In quantum information processing, the balance between the carrier lifetime and the carrier spin lifetime is crucially important for many envisaged implementations. It is thus extremely important to know and understand the relationship between the transient characteristics of a quantum dot and its emission wavelength.

![Figure 3.1: A typical PL spectrum for a single quantum dot exciton, recorded under identical conditions to the lifetime measurements presented in Section 3.2 (squares). The temperature was 4.1 K, the pump power was 50 nW, and the excitation source was pulsed at 76 MHz. A Gaussian fit (continuous curve) for the recorded data is also shown. The fitted linewidth was 0.056 nm, which is about 76 μeV.](image-url)
In this chapter, measurements of the photoluminescence (PL) lifetime of excitons in individual InGaAs/GaAs quantum dots are presented. The PL lifetimes were obtained using the time-correlated single photon counting method, as explained in Section 2.3. In particular, the dependence of this lifetime on the emission wavelength is studied. The measurements were performed using the sample described in Section 2.1, and the individual dots were isolated using a solid immersion lens. An example of a typical PL spectrum for a single quantum dot exciton is shown in Figure 3.1. The spectrum was recorded at 4.1 K, with a pump power of 50 nW, and using pulsed excitation, exactly as for the lifetime measurements presented in Section 3.2. The data also show typical values for the peak intensity and background contribution. Figure 3.1 also shows a Gaussian fit to the measured spectrum, revealing a resolution-limited linewidth of 76 µeV.

3.2 Dependence of lifetime on emission wavelength

Figure 3.2 shows the low-temperature (4.1 K) PL recombination times for individual quantum dots as a function of emission wavelength (filled circles), obtained using a pump power of 50 nW. The error bars show the estimated 95% confidence interval. Also shown is the ensemble luminescence spectrum (solid line). The recombination times were extracted from the data using the procedure described in Section 2.4. In all cases, the single exponential decay gave an almost flawless fit.

The dependence of the exciton recombination time on emission wavelength has been reported before with high-density InAs quantum dots\cite{31, 32, 33}, and individual thickness fluctuations in GaAs quantum wires\cite{34} and quantum wells\cite{35}, but not for individual self-assembled InGaAs/GaAs quantum dots.
The observed increasing lifetime with wavelength implies a decreasing oscillator strength. We wish to relate this to the often expected relationship between emission wavelength and dot size, to the effect that wider dots are assumed to emit at longer wavelengths. An increasing oscillator strength with dot size, however, was predicted theoretically by Takagahara\textsuperscript{36} for spherical dots larger than the exciton Bohr radius. This expectation, apparently contradictory to Figure 3.2, is supported by a number of experimental studies.

In reference 35, radiative lifetimes that decreased with emission wavelength were reported for ‘zero-dimensional’ size fluctuations in quantum wells, where the structures were larger in the lateral dimension, but smaller in height than the exciton Bohr radius. In
this study, as is widespread in the literature, the lateral size of the quantum dot is assumed to be a principal determinant of the emission wavelength, with larger diameter dots occupied by excitons of lower energy. In accord with theory\textsuperscript{36, 37}, it is argued that in this regime of sizes, larger than the exciton Bohr radius, the oscillator strength of the exciton transition is proportional to the ratio of the quantum dot volume to the volume of the exciton. Since the oscillator strength is inversely related to the radiative time constant, then this argument accounts for the observed trend, which is opposite to the trend in Figure 3.2. The tendency of the emission time to decrease with dot size has been observed in other diverse systems, such as CuCl nanostructures\textsuperscript{38} and colloidal CdSe nanocrystals\textsuperscript{39}.

In reference 35 it is also shown that when the dot diameter is less than the Bohr radius, the opposite trend is observed: shorter wavelengths correspond to faster emission. This observation matches calculations for flat disk-like dots by Andreani \textit{et al.}\textsuperscript{37}, predicting a minimum of the oscillator strength for a dot radius of about the Bohr radius.

For our dots, however, assuming an equal mix of In and Ga, the bulk Bohr radius can be estimated by averaging the two dielectric constants, $\varepsilon\varepsilon_0$, and the two reduced effective masses, $m^*$, and using the formula

$$a_B = \frac{4\pi\varepsilon\varepsilon_0\hbar^2}{e^2m^*}$$

(Equation 3.1),

(e is the electric charge and $\hbar$ is the reduced Planck constant, $\hbar/2\pi$) giving roughly 16 nm. This shows that we are clearly operating in the regime where the dot size ($\approx 70$ nm) is much larger than the exciton extension. As an upper limit, we could take pure InAs, for which the Bohr radius is 30 nm, still much less than the dot size. For such dots, we would expect to see the opposite trend to that shown in Figure 3.2, if the measured time constants represented only the radiative part of the decay process.

We will now show how several straightforward explanations for the tendency in Figure 3.2 can be excluded. In our PL spectra, the intensity measured on either side of an
exciton line is typically only marginally higher than the detector dark count, as shown in Figure 3.1, so we rule out any influence of background emission on the lifetimes. The emission times can conceivably be modified by radiative coupling between quantum dots. In this case, however, any enhancement of the emission rate is determined by the density of dots emitting at the same energy. This means that the emission rate would peak at the same wavelength as the luminescence, so this form of coupling is ruled out. Furthermore, our dot density is far too low for tunnel coupling between dots to modify the exciton survival times.

Evidence against phonon-assisted carrier escape and subsequent recapture can be found in Figure 3.3, showing temperature-dependent measurements of the ensemble full width at half maximum (FWHM). Spectra were recorded under macro-PL conditions at each temperature, covering a range from 800 to 1050 nm, thus including all the major luminescence features from the sample, which included the quantum dot ensemble, the wetting layer continuum, and a band of discrete states at energy just below that of the wetting layer. The spectra were fitted using three Gaussian functions, one for each of these major luminescence features (because of the macro-PL arrangement, the discrete states between wetting layer and dot ensemble appeared as a continuous feature), and the FWHM for the dot ensemble was taken from those fits. The error bars in the figure are the 95% confidence intervals provided by the fitting procedure.

For the ensemble, the emission linewidth was found to remain constant for temperatures below 40 K, before decreasing to a minimum at 100 K. The decrease in linewidth at temperatures above 40 K is explained by phonon-activated thermalization of the exciton population over the entirety of the available QD states. In this process, there is sufficient thermal energy to occasionally promote trapped electron-hole pairs back to the continuum, which happens with greater likelihood to the dots of higher energy (lower confinement potential). These free carriers then re-relax into other dots, which results in a higher proportion of the low-energy dots being populated. We are led to infer from
Figure 3.3 that this redistribution of carriers does not occur at 4 K, and therefore can not explain our observed temporal response.

![Graph of FWHM vs Temperature](image)

Figure 3.3: Full width at half maximum for the ensemble luminescence as a function of temperature. The error bars mark the 95% confidence intervals.

Figure 3.3 also provides empirical evidence against any tunnel coupling between dots, as tunneling would eliminate the need for thermal activation of the carrier redistribution. One can imagine a counter argument to this principle: if the dots are saturated by the pump at low temperature then any tendency for the carriers to redistribute among the dots is evidently eliminated. As the temperature is raised, however, we see a reduction of the integrated PL, indicating an activation of non-radiative recombination channels, which might bring the dot population below saturation level, enabling redistribution to occur. The spectra used to generate Figure 3.3, however, were recorded with a pump power of 1 µW, and power dependence measurements under
the same conditions revealed a still increasing integrated PL from the dots at a pump power of 10 µW, showing that this counter argument does not apply in the current case.

Note that while Figure 3.3 gives an impression that at low temperatures, increasing the temperature leads to a greater emission linewidth, it is more likely that a systematic error in the experiment is at fault. Glancing at Figure 3.2, it is evident that even in macro-PL measurement conditions, there is still considerable micro-PL character in the observed emission envelope: the dot density is low enough that we still see random fluctuations due to a locally varying distribution of dots. As the temperature is changed, the sample moves slightly under the microscope lens, and we must expect some changes to the sampled sub-ensemble. Where the systematic changes to the FWHM with temperature are least prevalent, such fluctuations must be expected to be most obvious, and this seems to be what is reflected in the low-temperature readings plotted in Figure 3.3.

The observed rising trend in emission times with wavelength also occurs repeatably in macro-PL measurements at various pump powers, though the range of time constants is typically less for the macro-PL experiments (about 650 ps at 900 nm to 750ps at 975 nm). This may be related to the necessity to pump the quantum dots harder, due to the lower detection efficiency in the macro-PL case, in which a low-numerical-aperture objective lens was used at a position on the sample laterally displaced from the solid-immersion lens. While the single-exciton measurements indicated some sort of non-repeateable (unique to each dot) temperature dependence of the lifetime, the macro-PL experiments showed no temperature dependence up to 50 K.

It has been observed\textsuperscript{33} that non-radiative recombination channels can have stronger effects on shorter wavelength dots, which could be invoked to explain the anomalous data in Figure 3.2, but the absence of any multi-exponential decays and the absence of any consistent temperature dependence of the decay constants rule out a great many of the known non-radiative processes.
3.3 Dependence of emission wavelength on dot height

An explanation for the observed wavelength dependence of the exciton lifetime is suggested by data on the diamagnetic shifts of quantum dots from the same wafer\textsuperscript{41}. These data, measured by N.A.J.M. Kleemans, are shown in Figure 3.4. The diamagnetic coefficients of individual QD excitons in a magnetic field applied along the growth direction were found not to vary significantly as a function of the emission energy. Since the diamagnetic coefficient is determined by the dimension of the exciton perpendicular to the applied magnetic field, the conclusion reached is that the dispersion of emission energies from the ensemble is not due to the dispersion of exciton diameters.

![Figure 3.4](image)

Figure 3.4: Measured diamagnetic coefficients for the quantum dots using out-of plane magnetic fields up to 10 Tesla. The error bars on these data (not shown) are approximately the size of the plotted symbols. These data are described in more detail in reference 41.
Assuming a parabolic potential for the quantum dot, a useful approximation of the diamagnetic coefficient, $\alpha_d$, can be obtained:

$$\alpha_d = \frac{e^2 d^2}{8m^*}$$  \hspace{1cm} (Equation 3.2),

where $e$ is the electron charge, $d$ is the exciton diameter, and $m^*$ is the reduced effective mass of the exciton. From this formula, it is clear that if the emission energy is determined by the exciton diameter, then any trend in Figure 3.4 must have a positive slope, while in reality the very slight tendency is downward. In fact, while the observed tendency is very slight, it is found to be highly statistically significant. Because the dots are wider than the exciton Bohr radius, changes to the dot width do not affect the lateral confinement, and hence the emission energy and diamagnetic coefficient are largely independent dot diameter.

Furthermore, if the emission energy was determined by the dot composition, then the diamagnetic coefficient would again change as a function of emission energy, due to changes to the exciton reduced mass. Where the In:Ga alloy ratio is concerned there are two competing mechanisms affecting the emission wavelength: (i) the straightforward tendency of the bandgap to approach that of unstrained GaAs as more Ga is incorporated, reducing the emission wavelength and (ii) the reduction of compressive strain as the Ga content is increased, due to reduced lattice mismatch with the GaAs substrate. This latter effect tends to reduce the emission energy of the dot. Thus there are two counter-acting influences on the emission wavelength, and it is not always clear which will dominate. The quantum dot sample used, however, is one of a series of samples grown at different temperatures, with more Ga intermixing occurring for the dots grown at higher temperature. It is also found that samples grown at higher temperatures exhibit shorter QD emission wavelengths, showing that for these dots increasing the Ga content reduces the emission wavelength. If the emission wavelength of a dot within the ensemble envelope was determined by the In:Ga alloy ratio, therefore, then the dots emitting at
longer wavelengths would necessarily have more In. Thus they would have lower exciton masses, and from Equation 3.2, their diamagnetic coefficients would be higher. Again we get the wrong sign for the slope of $\alpha_d$ as a function of wavelength, compared to Figure 3.4.

We argue instead that it is the dot height that dominates the exciton emission energy. Specifically, we infer that the dots emitting with longer wavelengths are those that have greater heights. A similar observation of near energy-invariant diamagnetic coefficients has also recently been reported for InAs/InP quantum dots\textsuperscript{42}. For this InP case, the ensemble luminescence was shown to consist of a number of overlapping peaks, which were found to correlate well with scanning tunneling microscopy (STM) measurements of the distribution of dot heights. This correlation allowed the features of the ensemble PL for these InAs/InP dots to be interpreted as a sequence of sub-ensembles, each populated by dots with heights equal to certain numbers of mono-layers.

The dots providing the data in Figure 3.2 have a diameter almost 20 times their height, and are also several times wider than the bulk Bohr radius. It is reasonable to propose therefore, that the oscillator strengths for these excitons are essentially those of a very narrow quantum well, with slight modification due to the weak lateral confinement. Keldysh\textsuperscript{43} has provided the theoretically derived oscillator strength for such a narrow quantum well with a finite barrier height, and he shows that it is inversely proportional to the well width. As the dot height increases, therefore, the oscillator strength would be expected to decrease, and the radiative lifetime would get longer, matching with our observations. Experimental results for quantum wells\textsuperscript{44} have also yielded exciton lifetimes that rise systematically with well thickness, for thicknesses smaller than or not much larger than the bulk Bohr radius.

It may also be that there is a height-dependent permanent dipole moment in these dots, affecting the carrier overlap, and therefore the lifetime, but no evidence is found in the literature that higher dots exhibit larger dipole moments. Regarding the scatter in Figure 3.2, it is likely that the variability of results at any given wavelength is governed
by a spread of lateral sizes, with the lifetimes in that case possibly conforming to the trend observed elsewhere\textsuperscript{33, 35}, and predicted theoretically\textsuperscript{36, 37}.

3.4 Conclusions

The emission lifetimes for individual InGaAs/GaAs quantum dots were measured over the entire emission range of the ensemble, and exhibited a strong rising trend with wavelength. This trend is opposite to that typically observed for other zero-dimensional structures. Our observations are well explained if the emission wavelength is predominantly fixed by the dot height, which is indicated by measurements of the dot diamagnetic coefficients, which show almost no systematic variation with emission wavelength.

A particularly difficult challenge in the study of semiconductor quantum dots continues to be the collection of combined optical and structural data on an individual dot, so that emission and morphological properties may be causally linked to one another unambiguously. STM provides an extremely powerful technique for assessing the structure and composition of an individual dot, but can not normally be combined with micro-PL measurements of the same dot, particularly when the optical properties of a buried dot are desired. By combining the lifetime measurements with observations of the diamagnetic coefficients of dots in the same sample, it has been possible to make progress toward a direct linkage of the optical and structural properties.

An obvious continuation of this program would be to measure both time-resolved PL and magneto-PL on the same individual dots. A further line of research that these presented results suggest would be to measure the diamagnetic shifts with the magnetic
field orientated parallel to the growth plane of the sample, so that the exciton extension in
the vertical direction is probed.
Chapter 4:

Double-peaked transient response of semiconductor quantum dots at high photoluminescence pump densities

Abstract:

Low-temperature time resolved photoluminescence is performed on individual InGaAs/GaAs quantum dots using high pump power excitation. Pumped well above saturation, the quantum dots are found to exhibit a double-peaked transient response to the pulsed pump laser. The normal emission feature at low power becomes substantially delayed by several nanoseconds at very high pump intensity. Additionally, a second decaying emission feature is found, reaching its maximum immediately after the high-power pump pulse is absorbed. This second feature is shown in spectrally and temporally resolved experiments to be due to the sample background emission. Various models are investigated to explain both the presence of the background and the delayed emission from the quantum dot exciton. We propose a model in which the background emission is assumed to be from carriers outside the dot, which perturb the excitonic binding, leading to sharp excitonic emission only after the background carriers have been removed from the system.
4.1 Double-peaked photoluminescence decays

In this chapter, the time-correlated single photon counting technique is applied to investigate the temporal evolution of the exciton population of single InGaAs/GaAs quantum dots that are optically pumped at a rate far above saturation. In photoluminescence (PL) studies of quantum dots, at low pump powers one finds that increasing the pump power leads to an increased photon detection rate. This results from the fact that increasing the pump power increases the probability to excite an electron-hole pair either in the dot (for resonant excitation) or spatially close to the dot (for excitation in the barrier). At a certain pump density, this probability ceases to increase as the pump power is raised, since the number of electron-hole pairs generated in the vicinity of the dot will be large enough to guarantee at least one exciton will form in the dot with each laser pulse. Above this pump density, the exciton is said to be saturated.

For dots that can accommodate more than one electron-hole pair, saturation of the single exciton is accompanied by growth in emission intensity for the biexciton, and so on for higher-order multi-exciton complexes, but these transitions are not degenerate with the single exciton, and so the emission rate at the single-exciton energy is still seen to saturate. The same argument holds for the multi-exciton emission lines, each of which is expected to also saturate at some pump power.

All experiments reported in this chapter were performed with a pulsed laser with wavelength of 765 nm and repetition rate of 76 MHz, and using a solid immersion lens to excite and collect PL from isolated quantum dots. Unless otherwise specified, the sample was maintained at liquid-helium temperature during the measurements.

PL from a typical quantum dot pumped at very high pump power are illustrated in Figure 4.1, which shows the time-averaged spectrum for a dot emitting at 915 nm, and pumped with a laser power 50 µW. This pump power is 3 orders of magnitude greater than that used for the low-power measurements of Chapter 3, where the dots were carefully pumped well below saturation, at only 50 nW. While we make this comparison,
we should note that though the precise pump density depends heavily on the incident pump power, differences in focusing capability and transmission of different solid immersion lenses used throughout the studies presented in this thesis make exact comparison of pump powers unreliable. While one dot may be found to be saturated with a particular nominal pump power, another dot under a different lens may be below saturation at the same laser power.

![Figure 4.1: Spectrum recorded for a quantum dot pumped at 50 µW using the pulsed laser. Saturation of a dot usually occurred at about 1 µW under these measurement conditions. Note the large background signal of nearly 2000 counts per second. The inset shows the evolution of the exciton (crosses) and background (circles) luminescence intensity as a function of pump power.](image)

The spectrum in Figure 4.1 was recorded on the charge-coupled device camera, but has essentially the same peak and background intensities as were found with a quick scan performed on the avalanche photo detector (APD). The pump wavelength was 765 nm. One of the most significant features of this spectrum is the high intensity of the
sample background. This background intensity is approximately two orders of magnitude higher than for the spectra found in the low-power studies presented in Chapter 3, and contributes a much higher fraction of the emitted photons than for the low-power cases.

The inset to Figure 4.1 shows how the intensities of the integrated exciton and the background emissions depend on the pump power. The values for the exciton are corrected by subtracting the average value for the background. While the background luminescence increases in intensity with a constant slope, the quantum dot intensity is seen to deviate substantially from a linear behaviour.

![Figure 4.2: Power-dependent PL transients measured on the 915 nm dot featured in Figure 4.1. The intensity is plotted on a logarithmic scale. At low pump power, the PL exhibits a simple, monotonic decay. As the power is increased, first the peak shifts to longer delays after the laser pulse, then a shoulder appears on the peak at short time delays, then this shoulder develops into a resolved peak, which eventually exceeds the maximum intensity of the later feature.](image-url)
Figure 4.2 illustrates the power dependence of the transient response of the 915 nm dot featured in Figure 4.1. At 0.5 µW, the lowest pump power presented, the build up and decay of the PL are essentially as was found for the low pump powers used in Chapter 3. At a slightly more intense pump of 1 µW, the build-up process is seen to be stretched out somewhat, pushing the peak intensity to a slightly later time. At 5 µW, the main peak is significantly delayed with respect to the laser pulse, compared to the lower powers, and a shoulder is beginning to emerge on the left-hand side of the main peak. Finally, at 50 µW pump power, the shoulder has become resolved into a distinct peak, which has even overtaken the intensity of the main peak. In anticipation, these two features of the high-power transients will be referred to as BG and X, as indicated on the figure. It is worth noting that for these and all other transients presented in this chapter, there has been no deconvolution of the data, and so the 650 ps timing uncertainty of the experimental setup should be born in mind.

Previous observations of the evolution of the luminescence decay of isolated quantum dots into two separate features at high pump power have been reported, aspects of which being explained variously by cascaded multi-exciton emission\(^\text{45, 46}\) and charge carriers surrounding the dot\(^\text{47}\).

The data in Figure 4.2 present two important questions, which the rest of this chapter will attempt to address:

1) Why does the original PL feature, X, become more delayed at higher excitation powers?

2) What is the cause of the BG feature that appears at short time delays when the pump power is raised?

None of the models in the literature referred to has succeeded in answering both these questions.
4.2 Spectroscopic investigation of the anomalous transient response

In the following, several experiments designed to constrain the set of possible explanations for the unusual phenomena depicted in Figure 4.2 are presented. The first simple investigation was to examine the temperature dependence of the high-power transient of a single dot. This is shown in Figure 4.3 for a quantum dot exciton positioned at 916 nm. The pump power was 50 µW for all the measured transients. The PL intensity decayed significantly as the temperature was increased, so longer accumulation times were employed for the higher temperatures. The curves are all divided by their corresponding accumulation times, however, to give a clear comparison.

Figure 4.3: Temperature dependence of the high-power transient PL for a quantum dot emitting at 916 nm. The pump power was 50 µW. Each data curve is divided by its corresponding accumulation time.
What is at low temperature the main feature of the decay in Figure 4.3, the peak at about 4.5 ns (X), is found to be more volatile than the earlier peak, at 2 ns, becoming substantially reduced in intensity at 60 K. The peak at 2 ns (BG), however, does not diminish in strength up to 60 K, suggesting that it originates from a physically very different source.

Figure 4.4 shows the time-integrated spectral scans of the emission line at the different temperatures used for Figure 4.3, and under the same pump conditions as for the measured transients. The scans were recorded on the APD. The sharp exciton peak on the spectra shows similar evolution, in terms of intensity, to the X feature in the transients, while the background intensity is seen in Figure 4.4 to be almost unaffected by temperature, similarly to the BG feature on the transients.

![Figure 4.4: Temperature dependence of the PL spectrum for the quantum dot exciton used for the transient measurements in Figure 4.3. Pulsed excitation was used, with constant integration time. The evolution of the peak intensity appears strikingly parallel to that of the second peak on the transient measurements, while the background count rate undergoes almost no extinction as the temperature is increased.](figure44.png)
The comparison between Figures 4.3 and 4.4 provides a strong suggestion that the two resolved features of the high-power transients originate from the quantum dot exciton, in the case of the delayed X peak, and from the sample background, in the case of the feature labeled BG. This hypothesis was tested by measuring the spectral dependence of the PL transience.

To determine whether the sources of the two peaks on the high-power transients are spectrally equally distributed, transients were measured at 3 µW pump power for a single line at 934 nm, using in each case a different monochromator slit width. First, the normal slit width of 50 µm was used, then the measurement was repeated with the width reduced to 30 and then 20 µm (both entrance and exit slit were reduced). Based on the grating dispersion and the focal length of the monochromator, the resolutions estimated for these slit widths are 98, 59, and 39 µeV, respectively. The results are plotted in Figure 4.5.

![Figure 4.5: High-power, low-temperature PL transients measured at different monochromator slit widths. The quantum dot used was located at 934 nm. The curves are rescaled so that the intensity of the second peak, at 3 ns, is the same on each histogram.](image)
The integration times varied for the different transients in Figure 4.5, but the 30 µm and 20 µm cases are rescaled to give the same intensity for the second peak, at 3 ns (the X feature), as for the 50 µm measurement. The relative intensity of the first transient peak is seen to be systematically reduced as the spectral selectivity of the detection setup is increased. This leads directly to the conclusion that the two peaks on the transient are from sources of different spectral width. The first transient peak (BG) is clearly produced by a spectrally much broader source. Recall that the second transient peak (X) is known from the power-dependent measurements to be from the quantum dot exciton itself. The finding from Figure 4.5 is consistent with the idea that the first peak on the high-power transient is from the spectrally quasi-uniform background emission.

![Figure 4.6: A spectral scan of the 928 nm emission line used for the spectrally resolved transience investigation presented in Figures 4.7 and 4.8. The vertical lines mark the monochromator grating positions used in the next two figures. These grating positions are 928.483, 928.516, 928.550, 928.616, 928.649, 928.682, 928.716, and 928.749 nm.](image)

To investigate further the spectral distribution of the features of the transient response, ten time-resolved measurements were performed with the monochromator
grating centered at different wavelengths in the region of a single quantum dot emission line, at 928.616 nm. The equally spaced wavelengths used spanned a range of about two linewidths of the dot on either side of the peak wavelength. The constant increment separating adjacent grating positions was 0.033 nm, and the lowest wavelength used was 928.450 nm. Figure 4.6 shows the time-averaged PL scan of the line, recorded using the APD, with vertical lines added to indicate the grating positions for all transient measurements but the first. The pump power was 10 µW.

![Figure 4.7](image-url)

**Figure 4.7:** High-power, low-temperature transients measured over a line at 928 nm. The pump power was 10 µW. The single measurement marked by a thicker curve was taken with the grating tuned to the point of maximum intensity of the quantum dot resonance. Other measurements were positioned symmetrically either side of the peak intensity, as indicated in Figure 4.6.

The transients recorded, also at 10 µW, at the grating positions indicated by the vertical lines in Figure 4.6 are depicted in Figure 4.7. Identical measurement conditions were employed for all the scans. All the transients, measured on and off the quantum dot PL position, exhibit almost identical BG peaks at just before 2 ns. This is the emission from the sample background. The intensity of a delayed X peak, at 4 ns, grows
systematically as the centre of the emission peak is approached. Paired transients, positioned symmetrically on either side of the central wavelength for the dot, also exhibit very similar evolution.

Figure 4.8 gives an alternative visualization of essentially the same data as in Figure 4.7. Here, the transient measured with the monochromator grating positioned at 928.450 nm, on the sample background, is subtracted from all the transients previously plotted. The transients on either side of the emission peak and furthest from the centre wavelength are almost completely flat, showing that the background emission does not vary in intensity or temporal behaviour in the region of a single quantum dot.

The other transients show essentially only the delayed quantum dot exciton luminescence, peaked at about 4 ns. This confirms that the first transient peak is produced by the background.
One other feature is worth noting briefly. Some of the curves in Figure 4.8 show suppression of the differentiated intensity close to the peak of the background, even producing negative values in some cases. The effect does appear to be systematic with spectral position, however, and is most probably due to fluctuation of the measurement process.

4.3 Modelling

At the end of Section 4.1, two questions raised by the observation of double-peaked quantum dot transients were posed. In the previous section, Section 4.2, a partial answer to one of these questions was obtained: we are now certain that the second peak that emerges at high pump power and at short time delays after the laser pulse is due to the sample background. We have not yet established, however, what the origin of the background emission is. In an effort to determine this and to answer the other question from Section 4.1, concerning why the exciton emission is delayed, three different models are considered, only one of which is found to be consistent with the current empirical facts. One of these models is the multi-exciton cascade theory, developed by Winger et al.\textsuperscript{48} to explain the peculiar properties of the cavity mode in a QD-photonic crystal cavity system, in which the dot is detuned slightly from the cavity resonance. This model is discussed in Section 4.3.1

The other possibilities that we investigate belong to a class of theory that shall be referred to as dressed-exciton models. One version of the dressed-exciton model that we consider invokes what we term the ‘game-over’ principle (Section 4.3.2), and attempts to answer specifically both the afore-mentioned questions. In this model, the sample is assumed to emit only one photon per laser pulse, either into the background or as sharply-
peaked exciton PL. Another implementation of the dressed-exciton concept (Section 4.3.3) treats the background emission as independent of the quantum dot, and is less prescriptive about its exact nature, but accounts qualitatively for the delayed appearance of the emission from the sharp exciton peak. The use of the term ‘dressed-exciton,’ here is not intended to denote a coupling between the exciton and the electro-magnetic field, as is one of its frequent uses.

4.3.1 Multi-exciton cascade model

The nature of the background emission from quantum dot samples has emerged as a crucial issue in experiments with dots in high-quality microcavities. This is due to the observation of a strong cavity mode in the emission spectra for these systems, even when the cavity resonance is detuned from any sharp quantum dot emission lines. The cavity mode, therefore, is interpreted as Purcell enhanced background emission.

Photon correlation experiments involving this cavity mode\(^4^9\) revealed that even though the cavity mode itself exhibits classical, uncorrelated statistics, the cross correlation between the cavity mode and an energetically nearby dot display strong antibunching. To resolve these seemingly contradictory observations, the multi-exciton cascade model was developed, and subjected to empirical tests with favorable results\(^4^8\).

In this model, the dot is initially populated with multiple electron-hole pairs, in any of various positive, negative or neutral charge states. Because of the large number of configurations for these multi-particle states, the transitions from \(n\) to \(n-1\) excitons, for \(n\) larger than 1, do not contribute sharp lines to the emission spectrum, but rather emit randomly into a broad background emission, clustered around the single exciton line. In cross-correlation experiments, therefore, detection of a single exciton recombination, after which the dot is empty, means that a background emission is not possible until the dot can capture sufficient carriers to populate one of these high-order manifolds, and the observation of antibunching follows. When the cavity mode is autocorrelated, however,
there is nothing to preclude the emission of a photon from the \( n = 3 \) to \( n = 2 \) manifold to be followed arbitrarily quickly by a photon from the \( n = 2 \) to \( n = 1 \) manifold, and there is consequently no observation of antibunching.

At first glance, this model might seem well equipped to explain both the strong background emission and the delayed emission of the single exciton that we observe. The reason these high-order manifolds can contribute to the cavity mode in the structures considered in reference 48, however, is precisely the fact that the cavity mode is not degenerate with the exciton. With our quantum dots, though, the background that we wish to account for is at the same energy as the sharp exciton peak. It is not to be expected that the \( n = 3 \) to \( n = 2 \) and \( n = 2 \) to \( n = 1 \) transitions, however, can be degenerate with the single exciton, which makes it difficult to attribute the present findings to this mechanism. Furthermore, it is worth noting that micro-PL spectra typical for our highly pumped dots differ markedly from those of the dots for which the multi-exciton cascade model was developed.

The micro-PL spectrum presented in reference 48 shows a dense cluster of emission lines, mainly due to a single dot, sitting on top of a broad pedestal of background emission. Figure 4.1, on the other hand shows a single emission line, and the background emission does not diminish with distance from the exciton. We do not see, therefore, any of the expected evidence of the multi-particle configurations that form the basis of this model. The applicability of this multi-exciton cascade process to explain the present data is consequently cast into serious doubt.

4.3.2 Dressed-exciton model: game-over scenario

The conception of this model, its mathematical formulation, and the analytical solution of the model’s equations were all performed by N. Chauvin to investigate a set of double-peaked transients observed for quantum dots in optical micro-cavities.
The idea of this dressed exciton model is as follows. The quantum dot is populated at all times by either one or no excitons. Pumped at high power, however, the material close to the dot is populated immediately after the laser pulse by several electrons trapped at defects, perhaps in the wetting layer.

The recombination time for the exciton inside the dot depends on the presence or absence of the surrounding charges, which are said to ‘dress’ the exciton. For simplicity, a binary set of values for the exciton recombination time can be taken, using a short time constant when the exciton is dressed by any number of charges and a longer time constant when no external charges are present.

The dressing charges themselves recombine with a time constant that is quite short. The exciton can thus recombine in either the dressed or undressed state. The initial feature in the PL transient is supposed to be from recombinations taking place in the dressed state, and the delayed peak is assumed to be due to recombinations when the dot is undressed.

Evidence that external carriers give rise to the background emission in this way is presented in reference 47, in which the cavity mode for a detuned dot-microcavity system was found to be extinguished by applying an electric field, while the exciton in the dot continued to emit. The cavity mode in this case, where the sharp transition due to the dot exciton is detuned from the cavity resonance, is found to be due to a Purcell enhancement of the background luminescence. The ability to remove this feature by applying an electric field, therefore, is seen as evidence that relatively free carriers, outside the dot, which can be swept aside by the application of a voltage, are responsible in some way for the background emission.

There is also a suggestion from measurements on several samples of different dot densities that delayed exciton emission at high pump power, similar to that reported here, is the result of carriers in the wetting layer. In this case, the lowest density samples exhibited the largest emission delays, which may be due to photo-generated carriers in these samples relaxing less easily into the sparser dots, and therefore remaining in the
wetting layer. The reason that relaxation is more problematic for the low dot densities is simply that there are few dots available to relax into.

In the current model, once the dot has been relieved of its single exciton, it is not repopulated until after the next laser pulse. This is what is meant by the ‘game-over’ concept. Only one emission from the system can take place for any given laser pulse. The exciton can emit either into the broad background, when the dot is dressed, or into the sharp exciton line, when undressed, but both can not occur after a single pulse. This assumption is necessary in order to reproduce the kinds of transients that have been presented in sections 4.1 and 4.2, in which the two features are clearly resolved. Any relaxation of this principle, allowing the exciton to become repopulated from the pool of external carriers, would broaden the timing uncertainty for the background and sharp-exciton emissions. This would cause the two features of the transient to blend into one another, giving transients with only one turning point, rather than the three turning points observed.

We need one other crucial assumption in order to allow these two transient features to become resolved. This concerns the effect of the external charges on the resonant energy of the dot. An exciton in any given dressed state is assumed to have its emission wavelength shifted, due to the Coulombic interaction with its environment. Furthermore, since the exciton in the dot can be dressed by different numbers of charges, trapped at a large array of possible locations surrounding the dot, the electrostatic environment of the dressed exciton is assumed to be random, giving rise to significant broadening of the emission line while these external charges are present. Thus with the high degree of spectral filtering provided by the monochromator, only a small fraction of the PL emitted during the dressed phase is collected at the detector, while the penalty for the undressed exciton, whose energy is well defined, is not so great. This is the reason why this model allows the observed double-peaked PL decay to be reproduced, rather than the second feature appearing merely as a weak afterthought as the first strong feature decays.
In this dressed-exciton model, therefore, the background emission (the BG feature referred to earlier) is considered to be broadened PL from the quantum dot exciton. This idea has particular appeal in the aforementioned observations from dots in micro-cavities, where the background was indeed observed as a broad pedestal surrounding the sharp resonance line\(^{47,48}\). Such pedestals are not observed, however, for the sample studied in the current work.

The other key feature of the dressed exciton model is that the observed delayed emission for the undressed exciton (X) is the result of the time taken for the photo- generated carriers surrounding the dot to recombine.

The mathematical formulation of this model makes use of three recombination rates, \(\gamma_d\), \(\gamma_{ud}\), and \(\gamma_{wl}\), which are respectively the dressed and undressed exciton recombination rates and the decay rate for the wetting-layer charges that dress the quantum dot exciton. In the rate equations that follow, \(P_{x,i}\) is the population probability of the exciton dressed by \(i\) external carriers:

\[
\frac{dP_{x,0}}{dt} = \gamma_{wl}P_{x,1} - \gamma_{ud}P_{x,0}
\]

(Equations 4.1)

\[
\frac{dP_{x,i}}{dt} = \gamma_{wl}P_{x,i+1} - (\gamma_{wl} + \gamma_d)P_{x,i}
\]

There are \(N+1\) such rate equations, where \(N\) is the number of external carriers in the vicinity of the dot immediately after the laser pulse is absorbed. The delayed PL feature in the measured transients, therefore, is modeled as the time-dependent solution of Equations 4.1 for \(P_{x,0}\):

\[
P_{x,0} = \left(\frac{\gamma_{wl}}{\gamma_d}\right)^N \left(e^{-(\gamma_{ud}t)} - \sum_{b=0}^{N-1} \frac{\gamma_d^b t^b}{b!} e^{-(\gamma_d+\gamma_{wl})t}\right).
\]
where $\gamma_t = \gamma_{wl} + \gamma_d - \gamma_{ud}$. The initial feature of the double-peaked transient is also seen to be just proportional to the total emissions by the dressed exciton, which is the detected background intensity:

$$I_{BG} \propto \sum_{a=0}^{n} \left( \frac{\gamma_t^a t^a}{a!} \right) e^{-(\gamma_d + \gamma_{wl})t},$$

where $n$ is an integer such that the background is only observed when the number of external carriers exceeds $N-n$.

Figure 4.9: Double-peaked transient for a quantum dot line at 915 nm, fitted using the solution to Equations 4.1. The main fitted parameters are indicated, along with the squared correlation coefficient for the fit.

This model was implemented in a least-squares fitting procedure, applied to the measured double-peaked decay curves, and provided very close fits to the data, demonstrating at least the utility of the mathematical structure of the model. An example of such a fitting is given in Figure 4.9. To evaluate the concepts behind the model, however, it is necessary to derive some testable hypothesis from the verbal description of the process just described. Since the background emission is modeled as luminescence

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from the quantum dot in a randomized electrostatic environment, and since the exciton is permitted in this model to emit only once per laser cycle, it can be readily seen that correlation experiments involving the background emission should exhibit antibunching, just like the quantum dot exciton itself. The background emission at a single wavelength was autocorrelated, and in a separate experiment, the background close to a sharp line from a dot was cross-correlated with the dot exciton, in attempts to demonstrate the antibunching that would corroborate this dressed exciton model.

![Autocorrelation of the background emission](image)

**Figure 4.10:** Autocorrelation of the sample background close to an emission peak at 915 nm. The pump power was 50 µW and the histogram resolution was 150 ps. The background intensity was 1800 counts per second, about 3 times the number of counts emitted by the quantum dot exciton.

The autocorrelation of the background emission was performed about 0.4 nm from the centre of a quantum dot emission peak at 915 nm. The pulsed pump power was 50 µW, and the background intensity was abut 1800 counts per second, approximately three quarters of the total intensity at the centre of the quantum dot peak (the quantum dot plus the background). The PL was passed to both APDs, and a histogram of coincidences
was obtained using a histogram resolution of 150 ps. The correlation, accumulated over two and a half hours, consisted of 44 sharp peaks, separated by the period of the pulsed laser. The average peak intensity at the maximum of each peak was 21 coincidences. The complete histogram is plotted in Figure 4.10. The peak at zero time delay is the one second from the right-hand edge of the histogram.

The peaks in Figure 4.10 were individually integrated, and some statistics obtained. First, the possibility of pile-up, explained in Section 2.3, was investigated. The averages for the first 18 and second 18 integrated peaks were compared and found to be quite similar, showing that the count rate is sufficiently low to ensure that random coincidences at very long time delays are not suppressed. The difference between the two averages was 10 counts, which is less than half a standard deviation, and in fact it is the peaks at shorter time delays that have the smaller average. This makes it valid to include the entire histogram in the analysis that follows.

The average number of integrated coincidences per histogram peak was found to be 438, with a standard deviation of 22. This dispersion matches the expected standard deviation for a Poisson distribution with the same mean. In fact a histogram of the number of peaks with each number of integrated counts overlaps well with this Poisson distribution, confirming that that histogram obeys the expected photon statistics, as shown in Figure 4.11. The average for the entire set of peaks was compared to the number for the peak at $\Delta t = 0$, which was lower by only 0.015 standard deviations, indicating that there is certainly no antibunching present.

A similar autocorrelation was performed on the background immediately adjacent to an emission line at 917 nm. The monochromator gratings were positioned 0.1 nm below the exciton resonance. The pulsed pump power was again 50 µW. The histogram resolution was set to 300 ps, giving 91 peaks on the entire histogram. Again, there was found to be no pile-up present in the histogram. The average number of integrated counts per peak was 203. The peak at $\Delta t = 0$ was found to be lower than average by only 0.012
standard deviations, which again precludes the occurrence of any antibunching for the background emission.

![Histogram of integrated peak areas](image)

**Figure 4.11:** Histogram of integrated peak areas for the correlation measurement in Figure 4.10. The smooth curve shows the theoretically expected distribution, obtained from a Poisson curve with mean equal to 440 coincidences, the average obtained from Figure 4.10.

A quantum dot emission line was located at 922 nm, and a cross correlation performed between the peak and the background, at a wavelength 0.1 nm lower than the peak. The Start signal was received from the monochromator tuned to the peak wavelength, while the Sync was obtained from the background emission. The pump power was 50 µW and the histogram resolution was 300 ps. Because the exciton transient consists of two peaks at this pump power, each part of the histogram consists of two peaks, and is the convolution of the background transient with that of the background and the exciton. The histogram was accumulated for nine and a half hours, giving about 40 coincidences at the maximum of the histogram feature. A close-up of this histogram around Δt = 0 is shown in Figure 4.12. The figure shows how the individual histogram
features are resolved into two peaks. The first of these peaks (peak 1) is dominated by the auto-correlation of the background, and the second peak (peak 2) consists mainly of coincidences between the background and the exciton. The reason that the features appear in the order that they do is that the histogram is reversed automatically, due to the reverse start-stop principle employed, as described in Chapter 2.

As described in Section 2.5, the location of the zero on the $\Delta t$ axis is estimated by autocorrelating a signal from a single detector. This location can be better fixed by then autocorrelating the pulsed laser on both detectors. The former measurement tells which peak of the histogram sits at $\Delta t = 0$, while the position of the maximum of that peak allows the position of the zero in Figure 4.12 to be fixed accurately.

![Figure 4.12: A small part of the exciton-background cross-correlation performed on a dot at 922 nm. The entire histogram consists of 91 peaks. The pump power was 50 $\mu$W.](image)
To analyze these two separate features of each histogram peak, regions of 11 and 16 histogram bins, corresponding to peaks 1 and 2, respectively, were integrated, and the resulting statistics were examined. The average counts for features 1 and 2 were 260 and 459, respectively. For peak 1, the $\Delta t = 0$ peak was found to be lower than the average by only 0.6 standard deviations and for peak 2, the $\Delta t = 0$ peak was found to be higher than average by 0.27 standard deviations. Neither of these deviations is statistically significant, when analyzed using Student’s distribution.

These results do not support the hypothesis that the background is produced by the same individual exciton as the sharp quantum dot peak. Due to the game-over principle, the $\Delta t = 0$ histogram feature should not contain any coincidences between the background and the exciton sharp line, as the system is not supposed to emit twice in one laser cycle. This means that the there should be no second peak on the $\Delta t = 0$ feature if this version of the dressed exciton model is to remain a viable explanation for the PL transients shown in Sections 4.1 and 4.2. The results of the autocorrelation and cross-correlation experiments, therefore, demand the rejection of this dressed-exciton theory, utilizing the game-over principle.

### 4.3.3 Dressed-exciton model: independent background emission

In the game-over scenario, the background emission was assumed to be produced by the same charge excitation, under different ambient conditions, as the sharp PL line. This was shown to be incompatible with photon correlation results, and any further attempt to utilize the dressed-exciton concept must do so without invoking the game-over principle. This is the program we now proceed to investigate.

We continue to treat the dot after each laser pulse as surrounded by a collection of charges, perhaps occupying an extended tail of the density of states of the wetting layer. The background emission is assumed to be most likely produced directly by the recombination of these external carriers, but is treated as predominantly definitely not
due to exciton recombination inside the dot. Due to their high density, these external carriers are supposed to form a plasma whose effect is to perturb the exciton binding of the electron and hole trapped in the dot, producing some correction to the energy of these carriers.

The spectral dependence of the background luminescence was measured using a pulsed pump of 3 µW. The monochromator grating was positioned far from any sharp emission lines, resulting in the data in Figure 4.13. These data are corrected to account for the detector dark counts and spectral sensitivity. They show that the power emitted by the background falls off approximately monotonically with distance form the wetting layer, supporting the hypothesis that the external carriers reside in a long wetting layer tail.

![Figure 4.13: Spectral dependence of the background emission intensity. Data recorded using a pulsed pump of 3 µW and corrected for dark counts and spectral response of detector.](image)

Emission lifetimes were also measured for the sample background as a function of detection energy, as shown in Figure 4.14. The observed lifetimes are found to be
predominantly significantly shorter than those for the quantum dot excitons, suggesting perhaps a two-dimensionally confined character. The observed increase in lifetime as the wavelength increases might, if the background is indeed due to a long wetting layer tail, be due to the very low density of states at longer wavelengths, making it harder for an electron and a hole to coincide at the same place, giving rise to longer lived carriers. Taken together with the temperature-dependent data in Figure 4.3, these data support the hypothesis that the background has an origin separate from the dots.

While the external carriers recombine, the time-varying Coulombic screening produces a broadening of the exciton emission that contributes very weakly to the background luminescence. Critically, no sharply peaked excitonic emission is seen during this period. Once the external carriers are removed from the system by recombination, however, the normal excitonic binding is restored and the sharp emission line becomes visible.

Figure 4.14: Emission time constants measured on the sample background at different wavelengths.
The problem of resolving the two features of the PL transients, for which the game-over principle was introduced earlier, does not arise in this situation. Because the number of external carriers can not be saturated easily by the pump laser, it becomes possible that the critical number of external carriers, below which the screening effect is removed, occurs quite late in the tail of the background decay. In this case, the occurrence of a minimum between the background and exciton transient peaks is quite straightforward to account for.

With the current model, the delay observed before the emission of the exciton is not real, but only apparent: the delay represents not the time taken to initiate emission, but the time taken for the emission to become detectable as that of a sharply peaked spectral line. A consequence of this interpretation is that the recorded intensity of the sharply peaked exciton PL should decrease as the apparent delay is increased by increasing the pump power. Figure 4.2 indeed shows a decrease in the maximum intensity of the delayed feature, marked X, as the pump power is increased from 5 to 50 µW. More data are needed, though, in order to establish the generality and functional form of this loss of recorded intensity with increased power.

A contrasting possibility is perhaps also worth mentioning, namely that it is the actual capture of carriers into the dot that is delayed by the presence of many external carriers. In such a case, the intensity of the sharply peaked luminescence would not be expected to decrease as the delay time increases, as described above. Generally, however, it is to be expected that the time required for the dot to capture carriers should be reduced, if anything, by increasing the number of carriers available.
4.4 Conclusions

The evolution of the transient PL response of an individual quantum dot as the pump power is increased has been studied. High above saturation, the PL transience exhibits two peaks. Power-dependent measurements show that the second peak on the PL transient is delayed emission from the sharply peaked exciton. Temperature-dependent and spectral investigations establish that the first transient peak is the sample background emission.

The general character of the PL spectrum of a quantum dot at high pump power is found to be inconsistent with treating the background emission as multi-excitonic recombination within the dot, as others have done with credible evidence.

Autocorrelation and cross-correlation experiments involving the background emission rule out a version of a dressed-exciton theory in which the background emission is again treated as emitted by the dot, but under a fluctuating Coulombic environment due to short-lived charge excitations that remain outside the dot. This model we have dubbed the ‘game-over’ hypothesis.

We propose another dressed-exciton model, in which the background emission is due directly to the carriers external to the dot. This hypothesis is supported by spectral and time-resolved investigations of the background PL, as well as temperature dependent measurements. The effects of the external carriers on the charges inside the dot are considered to be similar to those effects in the ‘game-over’ theory. The delay before onset of the recombination of the exciton is thought to be perhaps not a real delay, but rather an apparent delay, during which time the exciton energy is not well defined, and is consequently filtered efficiently by the monochromator.

Several follow-up investigations are suggested by these preliminary findings. To determine whether the delay of the exciton emission is real or apparent, further work could be performed to correlate the emission intensity of the sharp exciton peak with the delay – longer delays should produce lower photon counts, as later parts of the excitonic
exponential decay is being sampled. Also, a detailed theoretical formulation of the independent-background, dressed-exciton model would constitute valuable progress. To establish whether the background originates from the dots or from carriers in the host material, one might attempt to reproduce a similar sample with a wetting layer but no dots.

Other authors have, with credibility, assumed models for the origin of the background emission that are found to be inappropriate in the current studies. This suggests significant differences between the quantum dot samples investigated. It may be of considerable interest to enquire into the origin of these differences.
Chapter 5:

Nanosecond dynamics of the hyperfine interaction between electrons and optically-orientated nuclei in quantum dots

Abstract:
Time-resolved, low-temperature photoluminescence experiments were used to probe the dynamics of exciton spins in individual InGaAs/GaAs dots. Several of the studied dots exhibit the extraordinary feature of an exciton polarization increasing in absolute value with time. A number of key pieces of evidence are used to link this to the interaction between the electron spins and those of the nuclei, optically orientated by the pump laser. Small Overhauser shifts (< 10 µeV) have been measured in the absence of an external magnetic field and have been shown to be modulated systematically by changing the pump power. Rising polarization transients are also shown to be flattened by a similar reduction of the pump power. A model incorporating the hyperfine interaction with spin polarized nuclei is shown to reproduce the features of the measured exciton spin transients. This model points to a method to determine the degree of nuclear polarization in a quantum dot.
5.1 Introduction

This chapter describes measurements of the exciton spin dynamics in shallow InGaAs/GaAs quantum dots, using the time-correlated single-photon counting technique. All the reported experiments were conducted at a temperature of 4.1 K. As discussed in the introductory chapter, a material system with a long electron spin lifetime is highly desirable for proposed information-processing technologies. For optically transmitted quantum cryptographic keys encoded by photon polarization, relaxation of polarized electrons in a light emitting diode can in principle produce photons of the necessary strictly controlled polarization, provided the electron spin lifetime is much longer than its recombination time. For quantum computation, much longer spin lifetimes are probably required, owing to the fact that procedures such as quantum error correction demand something of the order of $10^4$ coherent operations to be performed before the electron spin loses coherence. There is, therefore, great interest in determining not only the spin-flip time scale in candidate material systems, but also the details of the mechanisms behind these spin flips, so that the spin-flip time can be lengthened.

In bulk semiconductors, one of the major spin-flip mechanisms is the spin-orbit interaction\textsuperscript{51}, and leads to picosecond exciton spin lifetimes\textsuperscript{52} that are far too short for quantum information purposes. In quantum dots, however, due to the heavy suppression of translational motion of the exciton, this mechanism is predicted to be greatly reduced\textsuperscript{53}. This results in the expectation, backed by considerable empirical evidence, that long spin lifetimes can be achieved, making quantum dots an interesting candidate for research. Two other spin-flip mechanisms emerge as important in quantum dots: (i) the exchange interaction between the electron and the hole and (ii) the hyperfine interaction between the electrons and the nuclear spins. This latter process is expected to dominate in many cases\textsuperscript{54}, making it particularly desirable to understand it well.

One of the most obvious and straight-forward ways to measure electron spin lifetimes in semiconductors is using time-resolved polarized photoluminescence. In low-
dimensional systems, such as quantum dots, the selection rules for optical recombination (Figure 5.1) allow exact mapping of the exciton spin onto the photon angular momentum.

In Figure 5.1, the possible recombination paths for an electron at the bottom of the conduction band (CB in the figure) to the top of the valence band (VB) are shown for materials such as GaAs and InAs. These selection rules assume that the photon emitted travels perpendicular to the growth plane. In bulk material, one-photon transitions are constrained to one heavy-hole level (hh) and one light-hole level (lh), for each spin state in the conduction band. Transitions ending at the heavy-hole level dominate, with a ratio 3:1, leading to a photon polarization of 50% from a population of electrons 100% polarized in the conduction band. In quantum dots, however, strain effects break the degeneracy of the heavy and light hole levels at $k = 0$, and reduce the light-hole energy sufficiently that all recombination terminate at the heavy hole. This leads to a photon polarization exactly equal to that of the CB electrons.

![Figure 5.1: Selection rules for InAs/GaAs quantum dots, for transitions where the photon emitted travels perpendicular to the growth plane.](image)

In Figure 5.1, the numbers beside each depicted level are the corresponding carrier angular momenta. Note that the spins of the valence-band levels are labeled...
according to the spin the electron will have once it has recombined with the hole at that level. This keeps the labeling consistent and facilitates our bookkeeping process: the $-\frac{1}{2}$ CB electron loses energy and an angular momentum of +1 unit to become a $-\frac{3}{2}$ VB electron. The energy difference and the +1 angular momentum are transmitted out of the semiconductor in the form of a $\sigma^+$ photon, as depicted in the figure. Note also that the traditional labeling of the photon helicity is eschewed, in favor of the more modern scheme, defining the photon angular momentum to be positive if its angular momentum vector points in the same direction as its linear momentum vector. The $\sigma^+$ photon thus carries $+\hbar$ angular momentum, and the labels in Figure 5.1 are immediately seen to add up appropriately.

The $|-\frac{1}{2},-\frac{3}{2}\rangle$ and $|+\frac{1}{2},+\frac{3}{2}\rangle$ excitons, consisting of, in the first case, a $-\frac{1}{2}$ electron and a $+\frac{3}{2}$ hole (recalling that the hole spin is opposite to that of the electron at the same level, before it was promoted to the conduction band), are termed ‘bright,’ as they recombine via the emission of a single photon. An alternate labeling for these bright exciton states is $|\pm\rangle$, corresponding to the sum of the electron and hole spins. It can happen, though, that a quantum dot finds itself populated by, for example, a $-\frac{1}{2}$ electron and a $-\frac{3}{2}$ hole. Here the difference in angular momentum is -2, and as long as these selection rules hold, recombinations excluding two-photon events, which are extremely unlikely, are forbidden. Likewise for the case whose angular momentum difference is +2. These $|\pm 2\rangle$ configurations are thus termed ‘dark excitons.’ The selection rules can be relaxed somewhat when states hybridize due to a reduction of symmetry, which can lead to the dark excitons producing an optical signature.55

The selection rules of Figure 5.1 also hold in reverse, governing the case of absorption. For strictly resonant optical excitation of a quantum dot using a 100% circularly polarized source, the maximum PL polarization is thus 100%, and is reduced
only by the exciton spin relaxation processes in the dot. In steady state, this reduced polarization is given by

\[ \rho = \rho_0 \frac{\tau_s}{2\tau_r + \tau_s} \]  

(Equation 5.1),

where \( \rho_0 \) is the initial polarization, \( \tau_r \) is the recombination time, i.e. the time taken for the population of excitons to reach \( 1/e \) times its initial value, and \( \tau_s \) is the spin flip time, characterizing the decay of a non-equilibrium spin population. Equation 5.1 is derived from a simple rate equation model

\[ \frac{d n^+}{dt} = aG + \frac{n^-}{\tau_s} - \frac{n^+}{\tau_r} \]

\[ \frac{d n^-}{dt} = (1-a)G + \frac{n^+}{\tau_s} - \frac{n^-}{\tau_r} \]

where \( G \) is the generation rate, \( 2a-1 \) is the pump polarization, and \( n^{+/}\) is the population of the spin-up/down exciton. This model assumes that the different spin states are degenerate, but can be generalized by inserting a Boltzmann factor to account for the effect of any energetic splitting on the equilibrium condition. The steady-state solution follows from setting the time derivatives equal to zero. It might be noticed that Equation 5.1 differs from some formulations in the literature, in that the recombination lifetime is here multiplied by 2. This is because a different definition of the spin flip time has been utilized: here, \( \tau_s \) characterizes the time taken for the occupation of either spin state to approach equilibrium, while for some other authors it gives the time for the average spin to evolve towards equilibrium, which is half as long as the time defined here.

For non-resonant excitation, where absorption of the pump light is in the bulk, the maximum exciton polarization and the maximum PL polarization are reduced to 50\%. The optical polarization, for the circular basis, is normally defined as:

\[ \rho = \frac{I^+ - I^-}{I^+ + I^-} \]  

(Equation 5.2),
where $I^{+/−}$ is the intensity of light polarized $σ^{+/−}$. This formula can also be adapted to define the exciton polarization etc.

A simple four-level rate equation model ignoring the hyperfine interaction (Figure 5.2) gives a good picture of how the quantum dot exciton spin often evolves. The equations describing this model are:

$$\frac{dB^+}{dt} = \frac{B^-}{\tau_b} - \frac{B^+}{\tau_b} - \frac{B^+}{\tau_c}$$

$$\frac{dB^-}{dt} = \frac{B^+}{\tau_b} - \frac{B^-}{\tau_b} - \frac{B^-}{\tau_c}$$

$$\frac{dX^+}{dt} = \frac{X^-}{\tau_c} + \frac{X^-}{\tau_s} - \frac{X^+}{\tau_s} - \frac{X^+}{\tau_r}$$

$$\frac{dX^-}{dt} = \frac{B^-}{\tau_c} + \frac{X^+}{\tau_s} - \frac{X^-}{\tau_s} - \frac{X^-}{\tau_r}.$$
where \( B^{+/−} \) are the populations of the \(|±1\rangle\) electron-hole pairs in the bulk, \( X^{+/−} \) are the excitons in the quantum dot, \( τ_b \) is the spin-flip time in the bulk, and \( τ_c \) is the capture time of the dot.

Considering a delta function excitation pulse, independent of the pulse that arrived before it, the coupled equations corresponding to the processes depicted in Figure 5.2 yield an analytical solution, which can be manipulated to provide the time dependence of the PL polarization for a given pump polarization:

\[
ρ(t) = ρ_0 \frac{\left( \frac{t}{τ_c} - \frac{t}{τ_r} \right) \left( -2τ_cτ_rτ_s + τ_b \left( -τ_rτ_s + τ_c \left( 2τ_r + τ_s \right) \right) \right)}{\left( e^{\frac{t}{τ_c}} - e^{\frac{t}{τ_r}} \right)}
\]

(Equation 5.3), where \( τ_b \) is the spin-flip time in the bulk, \( τ_c \) is the capture time of the dot, which also encompasses the time required for the exciton to relax to its ‘ground state,’ \( τ_s \) and \( τ_r \) are as before.

One thing that this model confirms, in line with basic intuition, is that \( ρ(t) \) does not get larger than \( ρ_0 \), but decays monotonically. One can further simplify the model by noting that the capture time for a quantum dot is usually very short and treating the exciton as generated directly in the dot. This reduces the four levels to only two, and eliminates the terms containing \( τ_b \) and \( τ_c \). In this case, the time dependent polarization is remarkably simple:

\[
ρ(t) = ρ_0 e^{\frac{-2t}{τ_s}}
\]

(Equation 5.4), which depends only on the spin-flip time, as should be expected. Here \( ρ_0 \) is still limited by the selection rules for absorption in the bulk material, giving 50 %. The reason why Equation 5.3 is dependent on \( τ_r \) is that the spin-flip times, \( τ_b \) and \( τ_s \), in the four-level
model are generally different. The probability at time t for a spin to have flipped, therefore, depends on its history, being different if the exciton was captured long before t than if it was captured immediately before t. If the $\tau_r$ is very short, for example, then the probability is high that the exciton was in the bulk soon before t.

It has been found on several occasions that PL polarization transients can be fitted by a single exponential, and Equation 5.4 has been implemented in a number of experimental studies of, for example, exciton spins in InGaAs quantum disks$^{56}$ and hole spin relaxation in negatively-charged CdSe/ZnSe quantum dots$^{57}$.

5.2 Spectroscopic analysis: absence of anisotropic exchange interaction

The spectral resolution of the PL setup used in these experiments is approximately 80 $\mu$eV, at the usual monochromator slit width of 50 $\mu$m. The spectroscopic experiments presented in this chapter, however, demonstrate a capability to resolve energetic splittings of excitonic emission lines of 5 $\mu$eV or less. This is possible because, as described in Chapter 2, the reproducibility of the position for a narrow peak has been measured to be less than 2 $\mu$eV. By careful analysis of the linearly polarized PL emission under linearly polarized excitation, it was possible to probe the magnitude of the anisotropic exchange interaction, discussed in the introductory chapter and expected to be present in InGaAs/GaAs quantum dots.

By repeatedly performing spectral PL scans on a single, isolated dot using different angles of a linear polarization analyzer for each scan, the splitting of the linearly polarized QD ground-state emission can be determined. As with all other reported experiments, the excitation wavelength for these PL scans was 765 nm, corresponding to a photon energy above the GaAs bandgap. Since it is not desired to presuppose the
emission basis of the expected linearly polarized PL, analyzer angles of 0, 20, 40, ...., 180 degrees were used, and the fitted peak position plotted against the analyzer angle was used to obtain the splitting.

A model curve composed of two orthogonally polarized Gaussian functions, separated by much less than their standard deviations shows that where the intensities and standard deviations are equal, the resultant peak position vs analyzer angle describes a \( \cos^2 \) function, repeating itself every 180 degrees. Relaxing the constraints so that the dispersions and amplitudes of the model curves are not equal can lead to the calculated plot of peak positions becoming more square-shaped and assuming an asymmetry between the widths of the concave-up and concave-down parts of the curve. Necessarily, though, the 180 degree periodicity is preserved.

When performing such linearly polarized experiments, it was found to be necessary to pay very careful attention to the behaviour of the linear analyzer. One of the analyzers used was found to introduce an angle-dependent displacement of the collected PL, appearing as an angle-dependent spectroscopic shift. Such shifts, however, were eliminated by performing further experiments with another polarizer, which in turn was verified by control experiments with a \( \lambda/4 \) plate inserted before the analyzer.

Scans were performed on more than a dozen sharp QD emission lines, using 20 or so data points over the width of the PL peak. Peak positions in nm were obtained to the fourth decimal place using the built-in peak-finder routine in the LabVIEW software program. This routine uses a quadratic fitting over sequential groups of points, with the user-defined number of points set to 20 in each case. The fitted peak positions did not differ from those obtained using a Gaussian model, found to be quite appropriate with regard to the line shape.

In no case was there found to be a periodic variation of the peak position vs analyzer angle, leading to the conclusion that there is no anisotropic exchange splitting larger than 2 \( \mu \text{eV} \) active in these quantum dots. This 2 \( \mu \text{eV} \) upper limit is certainly very tiny, with respect to the typical exchange energies measured for other quantum dots.
This finding is consistent with the observed ability to excite circularly polarized emission using a circularly polarized pump, discussed shortly, and with the findings from atomic-force microscopic (AFM) images of uncapped dots, grown under nominally identical conditions. The AFM images showed a circular footprint. As described in the introductory chapter, one of the major mechanisms believed to be responsible for the anisotropic exchange interaction in such dots is the reduction of symmetry due to an elongation along the [110] axis. No elongation along any axis was statistically evident for these dots, however.

5.3 Polarization transients

To measure the polarization transients, a linearly polarizing filter was placed before a λ/4 plate, in the path of the incoming excitation laser beam, and another λ/4 plate and linear analyzer were placed in the path of the collected PL. A particular polarization state was selected for the excitation, and PL was collected using two orthogonally polarized states to obtain the PL polarization from Equation 5.2. For measurements using the circular basis, the detected state was switched by rotating the wave plate by 90 degrees. For linearly polarized detection, the second λ/4 plate was removed.

To minimize the asymmetry between the two detected polarizations, PL was alternately accumulated for 1 minute with each angle of the λ/4 plate, and the process repeated over many cycles. This prevented any bias to occur due to the tendency of the PL intensity to decay with time. For the same reason, every time the PL intensity needed to be re-optimized, the order in which the detected polarizations were accumulated was reversed.
For the polarization transience measurements, the dots were pumped at 2 µW (unless otherwise stated), which corresponded to just below or just above the QD PL saturation point. For this reason, there was a significant contribution to the PL intensity from the sample background. To eliminate this from the polarization measurements, transients were also accumulated with the monochromator grating tuned to the flat part of the background emission, as close to the dot emission wavelength as possible. Background transients were obtained for both polarization states and subtracted from the corresponding transients measured at the wavelength of the QD peak. The sequence of measurements was, therefore, two 1 minute accumulations for one detected polarization (one at the QD wavelength followed by one at the background wavelength), followed by two similar 1 minute accumulations for the orthogonal polarization, repeated several times.

As we are not particularly interested in the exact labeling of the circularly polarized states used, and can not distinguish between \( \sigma^+ \) and \( \sigma^- \) anyway, an alternate labeling scheme is used to distinguish between the two unknown, but orthogonal circular states. The circular excitation and detection states will hereon be consistently referred to as \( \sigma^1 \) and \( \sigma^2 \). For the majority of the cases using a circular pump, the \( \sigma^1 \) state was employed. As the PL is collected in a backscattered configuration, and we would like the polarization to be positive for the usual case where the angular momenta of the incoming and outgoing photons have the same orientation, with respect to the laboratory, we define the polarization by:

\[
\rho = \frac{I^2 - I^1}{I^2 + I^1} \tag{Equation 5.5}
\]

where \( I^{1/2} \) is the intensity of the \( \sigma^{1/2} \) PL. This convention is adopted regardless of the polarization state used for the pump.

Using this circular basis for both excitation and detection, it was observed that the time-integrated PL is polarized by typically 25 % or less. The sign of the polarization is
positive for the $\sigma^1$ pump in nearly every case. The rare occurrence of negatively polarized PL will be discussed later, in Section 5.4.

Figure 5.3 shows the measured circular polarization transient for a sharp emission line at 940.48 nm, under $\sigma^1$ excitation. The polarization transient shows an unexpected feature: the positive polarization initially decays quickly, reaches a minimum, then begins to rise dramatically. In this case, the initial decay of the PL polarization is very fast, but in other cases, the polarization initially decays more slowly. The presence of a non-zero polarization at times earlier than the arrival of the excitation pulse is due to the nature of time-correlated photon-counting technique: rare events at times longer than the 13 ns period of the pulsed laser after the pulse that caused them appear at the beginning of the next pump cycle.

Background subtraction was achieved using separate transients measured on the sample background at 940.55 nm, 124 $\mu$eV lower in energy than the PL peak. The polarization transient measured at this wavelength is shown in Figure 5.4.

These transients, as with all the experimental transients shown in this chapter, have not been deconvoluted, and so the 650 ps experimental timing uncertainty should be kept in mind.

The background transient serves in this case as a reasonable check that the setup has been used to measure meaningful time-resolved polarization-dependent PL. The background polarization becomes high as the polarized excitation pulse is absorbed, then decays monotonically, towards zero. Unfortunately, the level to which the background eventually decays does not serve as a measure of the experimental polarization offset, as at long time delays after the pulse arrival, only the detector dark counts contribute to the signal, and are necessarily unpolarized.
Figure 5.3: Transient measurement of the background-corrected quantum-dot PL polarization (blue, continuous curve). Also plotted, for comparison, is the PL transient for the $\sigma^1$ detection (red, dotted curve).

Figure 5.4: The polarization transient for the sample background PL (blue, continuous curve), measured at an energy 124 $\mu$eV lower than the emission peak used for Figure 5.3. The PL transient using the $\sigma^1$ detection (red, dotted curve) is also shown.
Rising polarization transients similar to that in Figure 5.3 were observed for several other quantum dots, allowing further investigation of the phenomenon. The necessity to record the circular rather than linear polarization in order to observe the effect was quickly confirmed, and is consistent with the lack of any anisotropic exchange interaction. Results were also compared for similar measurements performed on the same quantum dot using in the first case a circularly polarized pump, and in the second case a linear pump, revealing the complete elimination of the effect in the linearly pumped case, as shown in Figure 5.5. This demonstrates clearly that the observed rising polarization transients are the direct result of the circular polarization of the pump laser, and are almost certainly, therefore, a result of optical orientation of charge carriers in the sample.

Figure 5.5: Comparison of the circular polarization transients measured using circularly (panel (a)) and linearly (panel (b)) polarized excitation. These measurements were performed on a single dot emitting at 930 nm, using identical measurement conditions in each case.
A further test was performed by comparing the polarization transients for a single dot, obtained using both $\sigma^1$ and $\sigma^2$ circularly polarized laser pulses. The results of such a test, performed on a dot emitting at 915 nm are shown in Figure 5.6. Both polarization transients plotted are calculated using the polarization defined by Equation 5.5. The two transients are essentially mirror images of each other, proving that the form of the transient is not due to some methodological error, but truly represents the evolution of the electron spins in the sample. The fact that two transients are positioned asymmetrically with regard to the x-axis is due to a systematic bias in the polarized detection.

It should be clear from the presented measurements that the use of Equation 5.1 to obtain the spin relaxation time from continuous-wave measurements of the PL polarization would be highly misleading in these circumstances.

There is one simple potential explanation for the observed oscillation of the exciton spin that can be quickly eliminated. Supposing for a moment that there was in fact an anisotropic exchange interaction active in the studied dots, then one could expect...
there to be spin quantum beats\textsuperscript{58} taking place. These oscillations of the exciton spin occur due to precession in the effective in-plane magnetic field resulting from the anisotropic exchange interaction. Calculating the periodicity for such oscillations, with reasonable values for the exchange energy, shows that the time scales provided by this explanation do not suit the current case, exemplified by Figures 5.3, 5.5, and 5.6. The expected angular frequency is given by the exchange energy divided by $\hbar$ (reference \textsuperscript{58}). Assuming an exchange splitting of only 20 $\mu$eV, this leads to an oscillation period of only 200 ps, which must be compared to the data above which could be argued to show a damped oscillation with a period of at least 6 ns. Even with an exchange energy of only 5 $\mu$eV, the calculated period is still below 1 ns.

5.4 Negatively charged excitons

Amongst the many quantum dots studied by polarized spectroscopy, two cases were discovered for which the PL polarization was opposite to that of the circularly polarized pump laser. Such counter polarizations have been reported several times before for quantum dots\textsuperscript{59, 60, 61, 62}, and are attributed to emission from negatively charged exciton complexes.

The reason for this counter polarized PL for negatively charged excitons can be illustrated by considering the case of excitation by $\sigma^+$ light, leading to the generation in the barrier material of a spin-down ($-\frac{1}{2}$) electron and a spin-up ($+\frac{3}{2}$) hole\textsuperscript{63}. The spin of the hole can be rapidly flipped in the bulk material due to strong spin-orbit coupling. If the quantum dot possesses a single resident electron, for example, then following capture of the photo-generated electron and hole, the charged exciton, labeled $X^-$, can assume a
number of different spin configurations. If the captured and resident electrons are of opposite spin, however, then the photon emitted upon recombination has a helicity that is uncorrelated with that of the photon initially absorbed, and contributes on average nothing to the measured polarization signal. Only the two cases, one bright and one dark, where the two electrons have the same spin ($-\frac{1}{2}$ in this case) retain a memory of the spin of the photo-excited electron. Such a parallel alignment of the electron spins is possible without violating the Pauli exclusion principle, provided that the photo-generated electron does not relax lower than the first excited state. The bright state corresponds to a hole that has remained un-flipped during the capture process, and produces PL co-polarized with the pump light. Due to anisotropic coupling, however, the bright state relaxes in a few tens of picoseconds by one of the electrons exchanging its spin with the hole. This flipped hole then determines the helicity of the emitted photon, leading to counter-polarized PL.

The time dependence of the PL polarization has been measured for negatively charged excitons\textsuperscript{64}, and is consistent with the above model. The observed polarization transients started positive (co-polarized with the pump) then quickly switched to negative, becoming more negative at later time delays.

There is good precedent, therefore, to attribute the counter-polarized luminescence observed in this study to negatively charged excitons. As the sample is nominally undoped, and as the PL lines studied contributed the dominant emission from the dots in question, then a simple statistical argument indicates that these are probably cases of $X^{-}$ excitons, each with a single resident electron.

The polarizations of the time-integrated PL measured for these two emission lines were -42 $\%$, for a line at 917 nm, and -35 $\%$, for a line at 927 nm. These polarizations are higher than the 25 $\%$ typical for the dots emitting PL co-polarized with the pump.
Figure 5.7: Measured transients for one of the X trions, emitting at 927 nm. The polarization (blue curve) is negative at all times. The time-dependent PL is also given (red, dotted curve).

For the 927 nm line, the polarization transient was measured (Figure 5.7). There is a suggestion in the figure that the polarization undergoes a slight relaxation from about 0.5 to 2 ns. It is possible that this behaviour is a signature of the same phenomenon responsible for the rising transient in Figure 5.3.

Further key measurements on these counter-polarized PL lines will be discussed later, in sections 5.5 and 5.6.
5.5 Overhauser Shifts

From the measured spin dynamics presented in section 5.3, it is clear that electron spins inside the quantum dots are in some cases evolving away from equilibrium at times long after the arrival of the polarized optical pulses. The electrons must, therefore, be in contact with some other reservoir of spins, itself either polarized or exchanging spins asymmetrically. Since there is no external magnetic field present, and time-inversion symmetry is upheld, then there should be no disparity in the rates of spin transfer for opposite spin states. One is led naturally, therefore, to consider the possibility that the observed electron spin dynamics is the result an exchange of angular momentum between spin-polarized nuclei and the electrons via the hyperfine interaction, and that these nuclear spins are themselves optically oriented via the same hyperfine interaction, in the presence of the circularly polarized pump light.

The possibility to align the spins of nuclei in metals using the hyperfine interaction with spin-polarized electrons was pointed out in 1953 by Albert Overhauser. Termed the Overhauser effect, this idea has been extended to semiconductors, and the possibility to achieve it in a solid by circularly polarized optical pumping of electrons was first demonstrated with silicon in 1967 by Georges Lampel.

The alignment of the nuclear magnetic moments by the hyperfine interaction produces a magnetic field that acts upon the electrons. Several experiments used electron spin resonance to establish the presence of this field. The development of optical spectroscopy of isolated quantum dots, however, made it possible to resolve the Overhauser shifts spectrally by PL experiments. This involves recording the modulation of the exciton Zeeman splitting in an external magnetic field under circularly polarized optical excitation. If the external magnetic field is parallel to the angular momentum vector of the incoming pump photons, then the optically orientated nuclear magnetic moments either add to or subtract from the external field. Compared to the unpolarized or linearly polarized cases, therefore, the Zeeman splitting of the exciton, given by $g \mu_B B$
(where \( g \) is the Landé factor for the exciton, \( \mu_B \) is the Bohr magneton, and \( B \) is the strength of the magnetic field), is either larger or smaller under circular polarization. This modification of the exciton emission energy by the nuclear alignment is termed the Overhauser shift. Whether this shift is positive or negative depends on the direction of the external field relative to the nuclear field and the electron g-factor.

The reason why the Overhauser shift is determined by the electron g-factor, rather than that of the exciton, is that the hole plays almost no part in the effect. Due to the p-like symmetry of the carrier wavefunctions in the valence band, the hole has a vanishing probability to be found close to a nucleus. Thus, there is very little direct exchange of spins between the holes and the nuclei and the holes experience almost no Zeeman effect due to the nuclear field.

The Overhauser shift has most often been observed in the presence of an external magnetic field, but it is in principle possible to observe it without, by registering small Zeeman splittings in circularly excited PL experiments. In practice, the usual occurrence of an anisotropic exchange interaction means that the eigenstates of the quantum dot neutral exciton are not the \(|\pm 1\rangle\) states, and orientation of the nuclear spins is not easily achieved, without an external magnetic field. Recently, two reports of measured Overhauser shifts for neutral excitons in quantum dots at zero external field have appeared. In both cases, the excitons exhibited clear exchange splittings in linearly excited PL, but switched to circularly polarized emission under a circular pump. In the first case, the observed nuclear alignment was attributed to the intermittent presence of the positive trion in the dot studied. In the second case, the Overhauser shift was ascribed to a brief period of a few picoseconds between capture of the electron by the dot and capture of the hole, during which the exchange interaction is, of course, not present.

In the present case, there is no need to invoke any such process to allow non-zero Overhauser shifts at zero external magnetic field, as the emission lines have already been demonstrated to be not subjected to an exchange splitting. Indeed, very small splittings of
the circularly polarized emission have been observed under circular excitation for numerous different quantum dots. These splittings are less than 10 µeV, which is admittedly much less than the 80 µeV spectral resolution, but they reverse sign under a change of the pump helicity, and disappear under linear excitation. These together firmly establish that the optically oriented carriers are resulting in an effective magnetic field in the sample. The observed changes in emission energy are also larger than the determined 2 µeV dispersion of the peak position, as described in Chapter 2.

An indication of the procedure and results that were typical of the dots studied is supplied by Table 5.1. Spectra were recorded under both $\sigma^1$ and $\sigma^2$ detection for three different pump states, linearly polarized and $\sigma^1$ and $\sigma^2$ circularly polarized. Changing the detection polarization was achieved by rotating the $\lambda/4$ plate by 90 degrees, rather than the linear analyzer. The peak positions were again fitted using the built-in peak-finder function in LabVIEW. The shift, $\Delta E$, is defined as the peak energy under $\sigma^1$ detection minus the peak energy under $\sigma^2$ detection. For each pump state, control measurements were performed to eliminate beam displacement effects due to the rotation of the $\lambda/4$ plate. These were performed by repeating the PL scans with the analyzer removed. Those scans that were controls are indicated in the fifth column of Table 5.1. The net shifts are simply the average shifts for the control measurements subtracted from the average shifts recorded with the analyzer in place. In this case, more measurements were performed for $\sigma^2$ pumped case, as the signal intensity was very low for these scans.

Table 5.1 indicates that the shifts under linear pumping are significantly smaller than either of the other shifts and not significantly different from zero. Table 5.1 also shows that the shifts for the $\sigma^1$ and $\sigma^2$ pumps are of opposite sign, and both show shifts that well exceed their associated error bars. These results have been repeated on several other dots. The natural conclusion drawn from these data is that there is indeed a weak Overhauser shift acting upon the studied quantum dots.
<table>
<thead>
<tr>
<th>Pump State</th>
<th>Peak Positions (eV)</th>
<th>(\Delta E) ((\mu)eV)</th>
<th>Net Shift ((\mu)eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sigma^1) detection</td>
<td>(\sigma^2) detection</td>
<td></td>
</tr>
<tr>
<td>linear</td>
<td>1.3729945 1.3729964 1.3730011</td>
<td>1.3729859 1.3729886 1.3729933</td>
<td>8.7 7.7 7.7</td>
</tr>
<tr>
<td>(\sigma^1)</td>
<td>1.3730032 1.3730005 1.3730032</td>
<td>1.3729927 1.3729876 1.3729962</td>
<td>10.5 12.9 7.0</td>
</tr>
<tr>
<td>(\sigma^2)</td>
<td>1.3729935 1.3729936 1.3729930 1.3729938 1.3729944 1.3729942</td>
<td>1.3729936 1.3729968 1.3729932 1.3729942 1.3729921 1.3729927</td>
<td>-0.2 -3.2 -0.2 -0.5 2.3 1.5</td>
</tr>
</tbody>
</table>

Table 5.1: Data on the spectroscopic shifts under a circular detection basis for a quantum dot emitting at 905 nm. The calculated net shifts indicate an Overhauser effect.

Spectroscopic shifts of the same kind were also measured for the two \(X^-\) trions discussed in section 5.4. Both of the cases were characterized by slightly stronger shifts than were achieved with the other dots. The measured \(X^-\) shifts were \(5.5 \pm 0.2 \mu\)eV for the 917 nm dot (only measured under \(\sigma^1\) pump) and \(6.5 \pm 0.7 \mu\)eV and \(-7.5 \pm 0.9 \mu\)eV for the 927 nm dot, respectively for the \(\sigma^1\) and \(\sigma^2\) pumps. The latter case of the 927 nm line was subjected to four separate measurements both with and without the linear analyzer, for all four combinations of circular pump and detection. The confidence intervals quoted are the convolutions of the errors for the normal and control measurements, given by \(C.I. = \sqrt{m^2 + c^2}\), where \(m\) and \(c\) are the standard deviations for the measurements and controls respectively. These error bars are therefore purely statistical, and can not account for systematic errors.

The \(X^-\) trion itself does not, of course, produce much polarization of the nuclei, due to the presence of two electrons in the dot of usually opposite spin. After the recombination of one of the electrons with the hole, however, the remaining electron can
provide an Overhauser effect, and does so very efficiently, provided that the dot spends more time occupied by the resident electron alone than by the trion. In the present case this is clearly the situation, as the laser pump period is 13 ns, while the exciton recombination time is of the order of a single ns. Thus the measurement of stronger shifts for the X\(^{-}\) trions supports the hypothesis of an Overhauser effect.

5.6 Power dependence

As indicated in the previous section, the proportion of time that the dot spends occupied by an electron makes a difference to the degree of nuclear polarization that can be achieved. This is because the eventual degree of nuclear polarization reached under stationary conditions is a balance between the hyperfine interaction, tending to align the nuclei, and the tendency of the nuclear alignment to decay towards equilibrium. Mechanisms contributing to the relaxation of the nuclear polarization could include interactions with unpolarized electrons, nuclear spin diffusion into the surrounding material, and the nuclear dipole and nuclear quadrupole interactions.

A corollary of this principle is that one should expect the degree of nuclear polarization under polarized optical excitation of charge carriers to decrease as the intensity of the excitation source is reduced. Such a dependence of the Overhauser shift on optical pump power has been observed for quantum dots on several occasions, for positive trions\(^{73}\), negative trions\(^{64}\), and neutral excitons\(^{74}\).

Due to the pulsed excitation used for the present study, a systematic reduction of the observed shifts with reduced pump power is therefore a good candidate as a means to verify that the observed very small shifts are real. Figure 5.8 illustrates the measured power dependence of the Overhauser shift for the X\(^{-}\) line emitting at 927 nm, discussed in
the previous two sections. These data clearly show a systematic modulation of the shifts that is consistent with the Overhauser effect. The effect is eliminated by reducing the pump power to 100 nW. Note that the highest pump power used, 2 µW, is just above the saturation point for this particular emission line, which is also consistently reflected in the leveling off of the dependence shown in the figure.

Figure 5.8: Pump power dependence of the Overhauser shifts measured for the X line at 927 nm

The data in Figure 5.8 can be reasonably interpreted as definitive confirmation that these dots undergo alignment of the nuclear spins, which reveals its signature in polarized PL measurements. Figure 5.8 also makes evident the range of pump powers in which this signature can be observed. To test the hypothesis that the rising polarization transients presented above result from this nuclear alignment, therefore, it is natural to compare transients for the appropriate high and low pump powers. This program is realized with the data presented in Figure 5.9.

Figure 5.9 shows that there is a clear difference between the high-power and low-power spin transients, for a dot emitting at 907 nm. The upper panel, recorded at the
usual 2 µW pump power, includes a distinct increase of the PL polarization at times later than 3 ns. In the lower panel, recorded with a pump power of 200 nW, at which the Overhauser shift is known to be almost absent, there is no rise in polarization, but rather the polarization decays monotonically towards equilibrium. This power dependence of the spin transience was confirmed with a repeat measurement on another dot emitting at 909 nm, and also serves as further evidence that the oscillating spin polarization of the dots is not a manifestation of quantum beating.

Figure 5.9: Power dependence of the time-resolved quantum dot exciton spin polarization. This dot was located at 907 nm. Panel (a): polarization and PL transience measured at a pump power of 2 µW. Panel (b): Equivalent measurement, with the pump power reduced to 200 nW.
5.7 Modelling

To demonstrate how it is possible for a polarization of the nuclei in a quantum dot to lead to neutral-exciton spin transients with a positive slope, a simple rate-equation model has been developed. A pictorial representation of this model is provided in Figure 5.10. This is an extension of the model depicted in Figure 5.2 to include the hyperfine process. The model again has four levels, ignoring the final state, which is the absence of any exciton. The necessary rate equations are:

\[
\frac{dB^+}{dt} = \frac{B^-}{\tau_b} - \frac{B^+}{\tau_b} - \frac{B^+}{\tau_c}
\]

\[
\frac{dB^-}{dt} = \frac{B^+}{\tau_b} - \frac{B^-}{\tau_b} - \frac{B^-}{\tau_c}
\]

(Equations 5.6)

\[
\frac{dX^+}{dt} = \frac{B^+}{\tau_c} + \frac{X^-}{\tau_{eh}} + \frac{NX^-}{\tau_h} - \frac{X^+}{\tau_{eh}} - \frac{(1-N)X^+}{\tau_h} - \frac{X^+}{\tau_R}
\]

\[
\frac{dX^-}{dt} = \frac{B^-}{\tau_c} + \frac{X^+}{\tau_{eh}} + \frac{(1-N)X^+}{\tau_h} - \frac{X^-}{\tau_{eh}} - \frac{NX^-}{\tau_h} - \frac{X^-}{\tau_R}
\]

In these equations, \(B^{+/-}\) represents the population of \(|\pm1\rangle\) electron-hole pairs in the bulk, \(X^{+/-}\) similarly represents the neutral excitons in the quantum dot. \(N\) is the fraction of the total number of nuclei in the dot that are oriented by an exchange of spin with the \(|\pm1\rangle\) exciton, \(\tau_{eh}\) is the time constant due to the electron-hole Coulomb exchange, and \(\tau_h\) is the time constant for the hyperfine interaction. All other quantities are as defined for the earlier model.
Figure 5.10: Model of the spin flip processes acting on the exciton during capture by and residence in the quantum dot. This model is an extension of the model in Figure 5.2, taking account of the hyperfine interaction. The size of the arrows is not intended to indicate the relative strengths of the processes.

There are no $|\pm 2\rangle$ excitons in this model, which is consistent with the exciton lifetime measurements presented in Chapter 3, in which it was shown that all quantum dot excitons studied could be modeled using a single exponential decay. The absence of dark excitons is probably related to a fast hole spin flip, which may follow from the rather shallow confinement provided by these quantum dots. For such shallow dots, we should expect the density of states for the holes to become more bulk-like.

The model in Figure 5.10 assumes that we are concerned with neutral excitons. From the co-polarization of pump and PL, we can be certain that transients such as that in Figure 5.3 are not due to negatively charged complexes, but we can not categorically rule
out positive trions. In fact, due to the bright-to-dark splitting for the neutral exciton, there is a problem with energy conservation at the moment that the electron exchanges spin with a nucleon, which might inhibit the hyperfine interaction. This problem would not arise for $X^+$ trions. Reference 72, however, indicates that it is possible to align the nuclei using optically oriented neutral excitons with no external magnetic field. In our case, due to the sample being undoped, it is highly unlikely that a majority of the studied emission lines would originate from positively charged excitons, and it is concluded that the excitons showing the rising polarization transients are most likely to be neutral. As the excitation power is quite high in the current experiments, it may be that energy conservation is provided by carriers external to the dot, whose presence is inferred in Chapter 4.

The above rate equations have been solved numerically using the Runge-Kutta method, and were found to reproduce the main features of the measured polarization transients. The suitability of treating the nuclear polarization, $2N-1$, as constant during each cycle of the pulsed laser is due to the build-up and decay times for the nuclear spin being much longer than the 13 ns laser period. Maletinski et al.\textsuperscript{75} found a build-up time of almost 10 ms and a decay time of 2 ms in the presence of a resident electron in the dot, or about 2 s in the absence of a resident electron. Decays times of 0.2 to 5 s were also measured for polarized nuclear spins by Makhonin et al.\textsuperscript{76}

In Figure 5.11 is shown the calculated spin polarization of the QD exciton for a fixed nuclear polarization of 40 % and an initial electron polarization of 50 %, this latter corresponding to a pump polarization of 100 % together with the selection rules for absorption in the bulk material. Reasonable values for the various time constants were employed, with the result that the feasibility to drive the electron spins away from equilibrium at times much later than the initial absorption of the pump pulse is demonstrated.
Several key features of the model can now be pointed out. (i) The electron-hole spin flip time is assumed to be much longer than the recombination time. (ii) The initial spin decay depicted in Figure 5.11 is due to the capture process. Reducing the capture time sufficiently eliminates the initial dip. (iii) The subsequent increase in spin polarization is caused by the hyperfine interaction. The increase can be made to disappear by increasing $\tau_{eh}$ or reducing $N$. (iv) In the limit that $\tau_{eh}$ is extremely long, the final polarization reached is found to be identical to the nuclear polarization. The final electron polarization is independent of all other parameters, including the helicity of the optical pump. In the real world, of course, the pump polarization will be instrumental in determining the degree of nuclear alignment. In Figure 5.11 the nuclear polarization is chosen arbitrarily to obtain a transient of the desired form. (v) The time constant used for the hyperfine interaction, 500 ps, matches exactly with experimental results for the spin
relaxation of electrons induced by interaction with a disordered ensemble of nuclear spins in InAs/GaAs quantum dots\textsuperscript{77}.

A number of reports concerning Overhauser shifts have included attempts to quantify the degree of nuclear polarization from the splitting of the $\sigma^+$ and $\sigma^-$ emission lines. In truth, however, determining the degree of nuclear polarization in this way is not possible without an additional measurement of the electron g-factor, as was carried out in reference 70. The transient spin measurements presented in this chapter, together with the model defined by Equations 5.6, point the way to a means to measure the nuclear polarization degree where one does not wish or is unable to measure or make assumptions about the electron g-factor. The required measurements, unlike those required for determining g-factors, can be performed in the absence of external magnetic fields.

Along with the success of this very simple model, there remain issues still to be resolved. Two issues in particular concern the rather high nuclear polarization assumed in order to generate the transience in Figure 5.11. The first problem is that with such strong nuclear alignment, one can expect effective magnetic fields in excess of 1 T. The small splittings observed, however, at such fields would require almost vanishing electron g-factors. While this is not impossible, one would expect that a sample of dots with near-zero g-factors would exhibit roughly equal numbers of positive and negative g-factors. For all the cases where Overhauser shifts were clearly recorded, however, the sign of the shift for a particular pump helicity is always the same.

The second challenge associated with the assumed nuclear polarization is that the model does not appear to supply any means to reach such a high degree of alignment. Starting from an unpolarized ensemble of nuclei, iterating the model many times, and incrementing the nuclear polarization after each simulated pump pulse, it was possible to estimate the build-up time and the steady-state polarization reached, for a given set of model parameters. Employing the parameters used for Figure 5.11, a minimum build-up time of a few milliseconds was obtained, assuming $10^5$ nuclei in a dot, but the stationary
value for the nuclear alignment was only 16 %, which can not supply such a noticeable recovery of the electron spin. There is clearly much yet to be understood about the nature of the measured rising transients, such as that depicted in Figure 5.3. It might be, for example that, operating at relatively high powers, the quantum dot nuclei are also pumped indirectly through hyperfine interactions taking place due to the many electrons generated in the bulk.

5.8 Conclusions

The dynamics of the exciton spins in single InGaAs/GaAs quantum dots has been measured by time-resolved polarized PL experiments. Several cases have been observed where the optically induced spin polarization initially drops, and then recovers, apparently stabilizing at some high value. The effect occurs under circularly polarized pumping only, and changes direction under reversal of the pump helicity.

There has been demonstrated to be no anisotropic exchange splitting for the dots, which is consistent with the ability excite strongly circularly polarized PL under circular pumping.

Small Overhauser shifts have been registered, and shown to be stronger for the negatively charged trion and to be reduced when the pump power is decreased, both in line with expectation. These shifts, as with the spin transients, were measured at zero external magnetic field. This Overhauser effect is direct evidence of optical orientation of the nuclear spins inside the quantum dots. It was also found that the observed power dependence of the spectral shifts was consistent with the power dependence of the spin transients: dots exhibiting rising spin polarizations at high pump power showed
monotonically decreasing spin polarizations at lower pump powers, at which the Overhauser shift was known to be greatly reduced or absent.

A rate-equation model showing the possibility to pump the electronic spins from an optically orientated nuclear bath has also been demonstrated.

Taken together, the evidence shows that the observed occurrence of exciton spin transients that evolve away from equilibrium as time increases is the result of the exchange of spins between the electrons and the optically aligned nuclear magnetic moments. This finding opens up the possibility to measure the degree of nuclear polarization by observing the temporal evolution of the exciton spin.

The Overhauser effect is one of the richest phenomena in the physics of quantum dots, and has inspired a great deal of experimental and theoretical research already. The results presented in this chapter have revealed another means to investigate the nature of this process.
Summary

Semiconductor quantum dots are objects with dimensions of a few to a few tens of nanometers. Confinement on such a small scale, of the order of the electron de Broglie wavelength, confers upon the charge carriers inside quantum dots a discrete energy spectrum. These atomic-like energy levels give rise to several technologically interesting properties. For example, laser diodes using quantum dots as their active medium offer the possibility of very low threshold currents, due to the near impossibility of coupling to electromagnetic frequencies apart from the lasing mode. The combination of discrete excitations and the high degree of spatial separation from the surrounding environment provided by quantum dots also makes it possible to maintain the electrons inside them in coherent states for much longer than with many other material systems, making quantum dots very suitable candidates for quantum information technologies. In particular the study of individual quantum dots has received a great deal of attention in recent years, with a view toward developing devices for quantum computing and quantum key distribution. In this context, an individual quantum dot is the critical component of many envisaged devices. In this thesis, several of the basic properties of individual self-assembled quantum dots are investigated. Chapter 1 gives a brief introduction to the technology of self-assembled quantum dots, and outlines several of the milestones that have been achieved in the field of single quantum dot research.

Time-correlated single photon counting, the central technique employed in this work, has been used to investigate the transient properties of photo-excited charges in quantum dots. This technique uses a sensitive photodetector, capable of registering single incident photons, to compare the arrival times of photons from the dots with a signal from a reference, allowing statistics that diagnose the transient luminescent properties to be built
up. The reference may be a voltage pulse produced every time the pulsed excitation laser fires, which could allow the spontaneous emission time to be determined, or the reference may be from another detector exposed also to the photoluminescence signal from the sample, which might permit one to examine the degree to which events inside the single dot can occur simultaneously. Chapter 2 gives more detail into the experimental techniques employed during this work.

The experimental work presented in this thesis is divided into three sections, (i) a study of the dependence of the spontaneous emission lifetime of a dot on its emission wavelength, (ii) an investigation into luminescence properties at high excitation powers, and (iii) a study of the transient interaction between electron spins in a quantum dot and the optically oriented spins of the nuclei of the dot. All these parts concern measurements of processes taking place within 10 ns after the arrival of a picosecond laser pulse.

Chapter 3 describes measurements of the recombination lifetimes of several dots from a single sample, each with a different emission wavelength. Due to the self assembly process, each dot possesses dimensions, composition, and geometry that differ slightly from those of all the others. This accounts for the different emission wavelengths and makes it desirable to understand how variations in these properties affect the luminescence behaviour. It was found that the emission lifetime gets systematically longer, as the resonant wavelength gets larger, which is opposite to observations by others for dots that, like ours, are wider than the exciton Bohr radius. We find that our dots are so much larger than the Bohr radius that the emission wavelength is uncorrelated with the lateral dimension of the dots, but is correlated closely with the height. This is shown by examination of the diamagnetic coefficients of the dots as a function of emission wavelength. We argue that the oscillator strengths of these dots must be treated as similar to those of narrow quantum wells, such that the lifetime gets longer as the structure gets thicker, i.e. as the dots get higher.
In Chapter 4, we examine photoluminescence transience at high excitation powers. Two findings in particular are described, (i) the exciton luminescence becomes delayed as the excitation power is increased, (ii) very strong background emission develops from the sample as the laser intensity is turned up. Three models are considered to account for these findings, (1) multiexciton emission, (2) dressed exciton emission, in which the background emission is actually from the exciton, but spectrally broadened by the presence of numerous charge carriers surrounding the dot, and (3) dressed exciton emission where the background emission is primarily from outside the dot, perhaps from a two-dimensionally confined continuum of states. In this latter case, the exciton emission from the dot is again broadened by the external carriers, becoming sharp only when sufficient of the external carriers have recombined. This leads to an apparent delay to the dot emission, brought about by the spectral filtering of the monochromator used in the experiments. This third mechanism is argued to be the most suitable explanation for the observations.

Chapter 5 details the study of spin excitations in quantum dots. Spins were excited in photoluminescence experiments using circularly polarized laser light. Photoluminescence decays were recorded for the cases co- and counter-polarized with the pump laser, and these were combined to give the transience of the spin state of the photo-excited exciton. Normally in such experiments, one expects a monotonic decay of the photoluminescence polarization, but with several of the dots studied in this work, the polarization was found to first decay, before rising again after a few nanoseconds. This phenomenon is linked by several experiments to the transfer of spins from the optically orientated nuclear spin reservoir, mediated by the hyperfine interaction. It is confirmed that the nuclei are indeed aligned by the polarized excitation light by recording small Overhauser splittings of the spectra of individual quantum dot emission lines. These splittings are displacements of the emission energy (about 5 µeV) of the co- and counter-polarized emissions, relative to
one another, when the circularly polarized excitation is used. The splitting changes direction, when the helicity of the excitation light is reversed. Next, the observed Overhauser effect is shown to exhibit power dependence, disappearing as the excitation power is reduced. Finally, the rising polarization transients, observed at relatively high power, are replaced by simple monotonic decays as the excitation is reduced to the level at which the Overhauser effect is known to be just vanishing. This last observation establishes clearly the role of the optically aligned nuclear spins in the observation of the rising polarization transients. A rate equation model is developed and used to demonstrate theoretically the feasibility to cause rising polarization transients by hyperfine interactions with optically oriented nuclear spins. The model shows that it should be possible to use measurements such as the reported transients to determine the degree of nuclear spin alignment in nuclear orientation experiments.
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References


41 N.A.J.M. Kleemans et al., unpublished


51. *Optical Orientation*, edited by B. Meier and B. P. Zakharchenya (North Holland, Amsterdam, 1984), Chap. 3


