THE ELECTRONIC AND OPTICAL PROPERTIES OF COLLOIDAL LEAD-SELENIDE SEMICONDUCTOR NANOCRYSTALS

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Jeffrey Matthew Harbold, Ph. D. Cornell University 2005

Quantum dots of the IV-VI semiconductors, and specifically lead selenide, strongly confine both electrons and holes, leading to a dramatic modification of the bulk semiconductor properties. This dissertation is devoted to the study of the electronic and optical properties of colloidal lead-selenide nanocrystals or quantum dots.

We begin by discussing the synthesis and characterization of high-quality colloidal lead-selenide nanocrystals with a narrow size distribution and well-passivated surfaces. With diameters between 3 and 8 nanometers, these lead-selenide quantum dots exhibit size-quantized transitions in the infrared region of the electromagnetic spectrum and exhibit bright band-edge photo-luminescence tunable from approximately 1000 to 2000 nanometers. These properties are extremely promising for applications.

The current theoretical understanding of the electronic states of IV-VI semiconductor quantum dots is based on envelope function approaches and tight-binding methods. While successful in explaining many features of the electronic structure, all current calculations fail to explain the presence of additional peaks in the optical absorption spectrum of lead-selenide and lead-sulfide quantum dots. We re-examine the leading explanations for these unexplained transitions and also consider a new possibility, that of enhanced

electric quadrupole transitions.

In addition, the degeneracy of the lowest optical transition in IV-VI quantum dots is predicted to split by the intervalley coupling of the 4 equivalent L-valleys in the first Brillouin zone. Low-temperature photoluminescence and size-selective photoluminescence experiments reveal, for the first time, a splitting in the emission spectra of lead-selenide and leadsulfide nanocrystals. These observations are consistent with a theoretical treatment of the splitting of the lowest transition in lead-selenide quantum dots due to intervalley coupling.

The dynamics of electrons and holes are crucially influenced by quantum confinement. In the strong confinement limit, a dramatic reduction in the excited state (or intraband) relaxation rate of carriers is predicted to occur. With its sparse electronic states and simple energy spectra, lead-selenide quantum dots represent an ideal material system in which to study the intraband carrier relaxation. We present the first measurements to directly time-resolve the intraband relaxation of electrons and holes in lead-selenide nanocrystals. Prior theories cannot explain the observed picosecond time-scale intraband relaxation and we discuss several possible explanations.

BIOGRAPHICAL SKETCH

Jeffrey Harbold was born in York, Pennsylvania in 1975 to Larry and Linda Harbold. Jeffrey first revealed his future scientific aspirations when, after a classroom demonstration by his second grade teacher Mrs. King, he announced to his parents, "I love science". Following high school, Jeffrey moved to Rochester, New York to attend the Rochester Institute of Technology from which he earned his B.S. in Physics in 1998. Still loving the climate in the Northeast, Jeffrey then entered the Ph.D. program in Applied Physics at Cornell University in Ithaca, New York. He joined the Wise research group in the summer of 1999 and spent the subsequent years learning about ultrafast lasers, nonlinear optics, and semiconductor quantum dots. Having surpassed his tolerance for snow and cold, Jeffrey will trade in his snow boots for flip-flops in January, 2005 as he pursues career and adventure on the beaches of Southern California. \circ To Mom and Dad

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Chapter 1 Introduction

1.1 Strong confinement in semiconductor nanocrystals

A nanocrystal (NC) or "quantum dot" (QD) is a small particle of a given material having the crystal structure of the corresponding bulk material but exhibiting vastly different electronic properties due to its small size. Quantum mechanically confining the electrons inside the QD leads to a change in the electronic states: the effective energy gap increases relative to the bulk material and discrete exciton states emerge.

The effects of quantum confinement on the electronic states were investigated theoretically by Efros and Efros.¹ They classified the size effects into three different confinement strength regimes- weak, intermediate, and strong- by comparing the radius (R) of the QD to the Bohr radius of the electron (a_e) and hole (a_h) in the parent bulk medium. The Bohr radii are defined as

$$a_{e,h} = \frac{4\pi \varepsilon(\infty)\hbar^2}{m_{e,h}e^2}$$
(1.1)

where $\varepsilon(\infty)$ is the optical frequency dielectric constant, and $m_{e,h}$ are the electron and hole effective masses.

In the case of weak confinement ($R > a_e$, a_h), the electron and hole retain their bulk-like character as an electron-hole pair bound by the Coulomb interaction (an exciton) and are virtually unaffected by the quantum confinement. In the intermediate regime ($a_e > R > a_h$), the electron is quantized and, as a result, experiences an increase in its energy (confinement energy). The hole is still unaffected by confinement and remains influenced by the Coulomb attraction to the confined electron. However, when the confinement is strong (a_{e} , $a_{h} > R$), both the energies are significantly increased due to quantum confinement. In fact, the energy of the strongly-confined charge carriers is often much greater than the energy of the Coulomb interaction. In this case, Coulomb effects are typically ignored.

According to Schmitt-Rink *et al.*, the optical properties undergo the greatest enhancement when the QD radius is smaller than the exciton Bohr radius, a_B

$$a_{\rm B} = \frac{4\pi\,\varepsilon(\infty)\hbar^2}{e^2} \left(\frac{1}{m_e} + \frac{1}{m_h}\right) \tag{1.2}$$

of the bulk semiconductor $(a_B > R)$.² This is based on the observation that as the dimensionality of the bulk semiconductor is reduced, the density of states becomes concentrated in narrowing energy bands and eventually discrete energy states. The effect this narrowing has on the strength of the transitions is profound; the oscillator strength of a strongly-confined electron-hole pair³ inside a QD is predicted to be a factor of $(a_B / R)^3$ times larger than that of the bulk exciton.² This implies that quantum dots in the strong confinement limit have the potential for greatly enhanced optical properties and motivates the study of semiconductor QDs in this limit.

For other phenomena, such as the excited state relaxation of charge carriers inside a QD, it is the confinement of the electrons and holes separately that matters. Little work has been done on QDs that strongly confine both the electrons and the holes (a_{e} , $a_{h} > R$). This regime requires either the synthesis of very small QDs or materials with large electron and hole Bohr radii.

Typically, QDs with a radius between 1.5 nm and 8 nm can be fabricated and attempts to make them smaller results in molecular clusters with a different crystal structure than the bulk semiconductor.⁴⁻⁷ As shown in Table 1-1, the problem encountered with II-VI and III-V semiconductors is that the hole Bohr radii are too small; in other words, the holes are too massive. Therefore, these materials do not allow access to the regime of strong confinement.

| | a _B (nm) | a _e (nm) | a _h (nm) |
|--------------------|---------------------|---------------------|---------------------|
| II-VI: CdSe | 3 | 3 | <1 |
| II-VI: CdS | 2 | 2 | <1 |
| III-V: InP | 9 | 7 | 2 |
| III-V: GaAs | 10 | 8 | 1 |
| IV-VI: PbS | 20 | 10 | 10 |
| <i>IV-VI:</i> PbSe | 47 | 23 | 24 |

Table 1.1: Exciton, electron, and hole Bohr radii of typical semiconductors used to make colloidal QDs.⁸

In contrast the IV-VI semiconductors, and in particular the lead-salt compounds, allow easy access to the strong confinement regime. Consider lead-selenide (PbSe) and lead-sulfide (PbS): the electron and hole masses are small and nearly identical.⁸ As shown in Table 1.1, this has the fortunate effect of leading to large Bohr radii for not only the electron and the exciton but the hole as well. Strong confinement can then be achieved in relatively large QDs, with a smaller fraction of their atoms on the surface. The



Figure 1.1: The general form of the bulk band structures and the electronic states that result when making a QD from (left:) II-VI and III-V semiconductors and (right:) IV-VI semiconductors.

properties of PbSe and PbS QDs are then far less likely to be influenced by surfaces effects like surface traps and defects.⁹

There are other advantages to working with IV-VI semiconductors as illustrated in Figure 1.1. In II-VI and III-V semiconductors, the confinement induced coupling between the three (heavy-hole, light-hole, and split-off) valence bands further complicates the already dense ladder of hole states and leads to congested energy spectra.^{10, 11} In contrast, the IV-VI semiconductors have simple non-degenerate conduction and valence bands. Additionally, their similarly small electron and hole masses lead to a large and nearly equal partitioning of the confinement energy between the both charge carriers. Ultimately, these attributes result in sparse electron *and* hole states and simple energy spectra.⁹

1.2 Organization of the dissertation

This dissertation is devoted to the study of the electronic and optical properties of colloidal PbSe QDs. In Chapter 2, we discuss the synthesis and characterization of high-quality colloidal PbSe nanocrystals. Prior to this work, the best available lead salt nanocrystals were monodisperse and brightly-emitting PbSe QDs in a glass host.¹² The colloidal synthesis presented here, based on the recent work of Murray and coworkers,¹³ represents a significant advancement in the growth of IV-VI NCs with well-controlled size, a narrow size distribution, and well-passivated surfaces. With diameters between 3 and 8 nm, these PbSe QDs exhibit size quantized transitions in the infrared region of the electromagnetic spectrum and exhibit bright band-edge



Figure 1.2: The general form of the first few electron and hole energy levels of PbSe or PbS QDs. The states are labeled (right side) by the quantum numbers j (total angular momentum) and π (parity). An alternative scheme (left side) labels the states by the orbital angular momentum of the envelope function. The lowest several dipole-allowed transitions are also depicted.

photoluminescence tunable from approximately 1000 to 2000 nm. These properties are promising for applications in optoelectronics and microscopy. In particular, PbSe QDs might enable a broadband and tunable optical amplifier for telecommunication wavelengths.

As a brief introduction to the electronic structure of these materials, the general form of the first few electron (e) and hole (h) energy levels of PbSe QDs or PbS QDs are shown in Figure 1.2. The states are labeled by total angular momentum (j) and parity (π), but for simplicity we adopt the usual convention by referring to the states according to the angular momentum of the envelope function ($\ell = 0, 1...$ as S, P,...). The 3 lowest calculated dipole-allowed transitions ($1S_e - 1S_{h'}$ $1P_e - 1P_{h'}$ and $1D_e - 1D_h$) are also indicated.

The current theoretical understanding of the electronic states of lead salt QDs is based on envelope function approaches^{14, 15} and tight-binding methods.¹⁶ Conceptually, the envelope function approximation treats the QD as a truncated infinite crystal. It assumes that the QD wavefunction may be expressed as a product of the bulk semiconductor wavefunction and an envelope function that independently satisfies the physical QD boundary conditions. On the other hand, the tight-binding approximation is an atomistic approach. It assumes that the QD wavefunction may be expressed as a sum over the wavefunctions of the individual atoms comprising the QD when only accounting for nearest-neighbor interactions. These electronic structure calculations have been very successful in providing accurate energies of higher exciton states as well as the lowest exciton, electron and hole wavefunctions with the correct symmetries, and the interband dipole transition strengths and selection rules.



Figure 1.3: The direct band gap of the IV-VI semiconductors occurs at the 4 equivalent L-points of the Brillouin zone.

Despite these successes, all current calculations fail to explain the presence of additional structure in the optical absorption spectrum of PbSe and PbS QDs.¹⁷⁻¹⁹ In Chapter 3, we re-examine the leading explanations for these unexplained transitions in light of recent experimental results. We also consider a new possibility, that of enhanced electric quadrupole transitions.

There is another level of complexity to the electronic structure of IV-VI semiconductor NCs not yet mentioned. As depicted in Figure 1.1, the direct energy gap occurs not at the center of the Brillouin zone (Γ) but rather at the 4 equivalent hexagonal face-centers (L), see Figure 1.3.²⁰ Therefore, the degeneracy of the electronic states is increased by factor of 4. This source of degeneracy in PbSe and PbS is expected to be lifted by coupling of the equivalent valleys but to date, there is no experimental evidence of this effect.

One possible explanation why this and other fine structure has not been observed is that in ensemble measurements of QDs, the inevitable distribution of sizes leads to a broadening of the observed spectral features. There are several sophisticated spectroscopic techniques that can circumvent this source of inhomogeneous broadening^{6, 21, 22} however, one relatively simple emission spectroscopy technique can also reduce the broadening effect of the size distribution. In size-selective photoluminescence (PL) experiments, only the subset of largest-sized QDs are excited, leading to a narrowed emission spectrum.²³

In Chapter 4, we present the results of PL measurements on colloidal PbSe and PbS QDs. At low temperatures, a splitting is observed in the emission spectra. The magnitude of the splitting increases as the dot size is decreased in agreement with calculations of the splitting of the lowest transition due to inter-valley coupling.¹⁶ We also present size-selective PL measurements on

colloidal PbSe and PbS QDs that reveal broad emission lines even when the inhomogeneous broadening effects of the size distribution are eliminated suggesting that the degeneracies arising from the different valleys are also split by other mechanisms.

As mentioned earlier, the dynamics of electrons and holes are crucially influenced by quantum confinement. In the strong confinement limit, a dramatic reduction in the excited state (or intraband) relaxation rate of carriers (see Figure 1.2: for instance, 1P_e to 1S_e and 1P_h to 1S_h) is predicted to occur.^{24, 25} With its sparse electronic states and simple energy spectra, PbSe QDs represent an ideal material system in which to study the intraband carrier relaxation. In Chapter 5, we present the first measurements to directly time-resolve the intraband relaxation of electrons and holes in lead-selenide nanocrystals. Prior theories cannot explain the observed picosecond time-scale intraband relaxation and we consider several possible explanations of how the "phonon bottleneck" to carrier relaxation is bypassed.

This dissertation concludes in Chapter 6 with some thoughts on future directions for research on IV-VI semiconductor NCs.

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Chapter 2 The synthesis and characterization of colloidal PbSe nanocrystals

We present the structural and optical characterization of colloidal PbSe nanocrystals. With diameters between 3 and 8 nm, the lowest-energy exciton transitions in these structures occur at wavelengths between 1.00 to 1.85 μ m. Band-edge luminescence spectra with quantum yields as high as 80% are observed. Unexpectedly long (~300 ns) luminescence lifetimes are observed. These properties are promising for applications in optoelectronics and microscopy.

2.1 Introduction

Colloidal II-VI and III-V semiconductor quantum dots (QDs) have attracted much attention due to their interesting electronic and optical properties and potential for a wide range of applications. For example, CdSe nanocrystals have shown potential as superior biological labels,¹⁻³ improved organic-inorganic hybrid solar cells,⁴ white-light laser sources,⁵⁻⁷ and tunnel diodes,⁸ while InAs QDs have demonstrated potential as near IR emitters⁹ and as nanometer scale components for molecular electronics.¹⁰

The exciting potential of these quantum-confined materials arises from the fact that it is possible to fabricate structures of radius *R* smaller than the electron-hole-pair (exciton) Bohr radius a_B . Although the exciton in II-VI and III-V QD materials can be strongly confined, there is a significant asymmetry

between the individual charge carriers owing to the large difference in their effective masses. The Bohr radius of the hole in most II–VI and III–V materials is ~1 nm, so it is effectively impossible to achieve strong confinement of the hole.

QDs of IV–VI materials such as PbS and PbSe offer unique access to the regime of extreme quantum confinement since the electron, hole, and exciton all have relatively large Bohr radii.¹¹ In PbSe, the electron, hole, and exciton Bohr radii are 23, 24, and 47 nm, respectively. These large radii allow strong confinement to be achieved in relatively large structures. Thus, QDs of IV-VI materials may have properties reflecting all the benefits of strong quantum confinement, with reduced influence from surface effects; for the same level of confinement as QDs of II-VI or III-V materials, the surface-to-volume ratio can be quite low in IV-VI materials. Furthermore, these large Bohr radii also allow for materials to be fabricated with much stronger quantum confinement than is possible with II-VI or III-V materials.¹² Indeed, studies of extremelyconfined IV-VI QDs have revealed that these materials have unique vibrational modes,¹³ can exhibit extremely weak electron-phonon coupling,¹⁴ have negligible exchange and Coulomb energies,¹⁵ and can have a temperature-independent band-gap.¹⁶ Lead-salt quantum dots are among few materials that can provide size-quantized electronic transitions at technologically-important infrared wavelengths. These structures may find use in optoelectronic applications as well as in biophysical applications such as fluorescence microscopy.

Despite the potential advantages of working with QDs in the extremely strong confinement limit, IV-VI QDs have received relatively little attention. This is partially due to the difficulty of synthesizing colloidal quantum dots with a well-controlled size, narrow size distribution, and well-passivated surface. Monodisperse PbS¹⁷ and PbSe¹⁸ QDs have been produced in glass hosts. However, some applications will benefit from the processability of colloidal solutions. Recently, the synthesis of high-quality colloidal PbSe QDs was reported by Murray and co-workers.¹⁹ Electron microscopy and optical absorption spectra show that monodisperse QDs of controllable mean size were produced.

Here we describe the synthesis and characterization of colloidal PbSe quantum dots. Sizes ranging from 3 to 8 nm in diameter are produced with narrow size distributions. The ratio of quantum dot to exciton radii R/a_B is a measure of the degree of confinement, and is very small: R/a_B ranges from 0.07 to 0.2 for these quantum dots. The structures exhibit clear exciton peaks in absorption and bright band-edge luminescence.

2.2 Synthesis

PbSe quantum dots were synthesized according to modified versions of the literature methods¹⁹ by Dr. H. Du in the Krauss group in the Department of Chemistry at the University of Rochester. The reaction consisted of a single-flask, single-injection synthesis based on techniques described by Murray *et al.*¹⁹. Trioctylphosphine (TOP) was purchased from Fluka, and all other reagents were purchased from Aldrich. For a typical synthesis, 1.5 g of lead acetate and 5.1 ml of oleic acid were dissolved in 25 ml of phenyl ether. The reaction mixture was heated up to 140°C for 1 hour under stirring, under a continuous flow of nitrogen, and then cooled. When the temperature of the phenyl ether solution fell below 70°C, 12 ml of 1-M trioctylphosphine selenide

(TOPSe) was added to the flask thereby forming the molecular precursor solution. The precursor solution was subsequently loaded into a 50-ml syringe and was rapidly injected into a flask containing 40 ml of vigorously-stirred phenyl ether under a continuous flow of nitrogen. The injection and growth temperature was varied from 80°C to 150°C to obtain the desired particle size. Higher injection and growth temperatures were used to prepare larger-size QDs. After injection, the reaction mixture was maintained at the growth temperature for 5 to 10 minutes, and then the colloid was cooled to approximately 40°C and stored in hexane.

2.3 Experimental results

The quantum dots were characterized by X-ray diffraction, scanning transmission electron microscopy (STEM), optical absorption spectroscopy, and fluorescence spectroscopy. Samples were prepared according to the following procedure. PbSe quantum dots were precipitated from hexane with a butanol/methanol mixture and centrifuged in order to remove excess TOP, oleic acid and phenyl ether. After repeating this procedure twice, the solid PbSe QD pellet was dissolved in tetrachloroethylene. Provided favorable conditions of temperature, injection and nanocrystal growth time were employed, size-selective precipitation was not necessary to obtain narrow size distributions.

Powder X-ray diffraction was performed at room temperature on a Philips Multipurpose Diffractometer, using copper $K\alpha$ 1 radiation (0.154056 nm). Samples were prepared by evaporating several drops of the PbSe nanocrystal sample onto a special low-background X-ray sample holder plate. STEM



Figure 2.1: X-ray diffraction pattern of PbSe QDs indexed to the bulk-rock salt crystal structure. The peaks labeled (*) are due to trace amounts of the unreacted precursor, lead oleate.

samples were prepared by depositing a ~20- μ l drop of the colloid in hexane or tetrachloroethylene on a holey carbon film on a 300-mesh copper grid. A Vacuum Generators HB501UX scanning transmission electron microscope operating at 100 keV and equipped with a high-resolution pole piece was used to acquire the STEM images. Bright-field and annular dark-field images were simultaneously acquired using software developed at Cornell University.²⁰

Absorption spectra were recorded on a Perkin-Elmer UV/VIS/NIR Spectrometer (Lambda 19). Fluorescence spectra and quantum yield (QY) measurements were performed on modular research fluorescence system from Acton Research. Fluorescence was collected at right angle to the excitation and detected with an InGaAs photodiode. For fluorescence measurements, care was taken to limit the optical density at the lowest exciton of all samples to <0.1. The laser dye IR 125 (which has a QY of 13% in dimethyl sulfoxide²¹) was used as a standard for determining the quantum yield of the PbSe quantum dots. Fluorescence decays were recorded using time-correlated single-photon counting (PicoQuant FluoTime 200). A pulsed diode laser (880 nm wavelength) was used for excitation, and a cooled Ge avalanche photodiode recorded the time-correlated signal.

PbSe quantum dots of different diameter were obtained by varying the growth temperature of the solution. Temperatures of 80 to 150 °C were used to continuously tune the nanocrystal size from 3 to 8 nm. The x-ray diffraction trace in Figure 2.1 exhibits clear peaks that confirm the rocksalt crystal structure with the lattice constant of bulk PbSe. From the widths of the diffraction orders we estimate the nanocrystal sizes, and these are consistent with the result of electron microscopy. A typical low-magnification annular-darkfield STEM image (Figure 2.2) shows an ensemble of PbSe QDs assembled



Figure 2.2: Low-resolution STEM micrograph of PbSe QDs (full scale= 320 nm) showing the ordering of an ensemble of NCs.



Figure 2.3: High-resolution STEM micrograph of a PbSe QD (full scale= 6.4 nm) revealing lattice imaging of the NC.

into a locally well-ordered close-packed array. The fact that ordered closepacked structures are observed demonstrates that the PbSe QDs have a wellcontrolled size and shape. Figure 2.3 shows a high-resolution STEM image of a single PbSe QD ~7 nm in diameter. A hexagonal array of columns of Pb atoms is clearly visible in the image, showing that the synthesis produces singlecrystal nanoparticles free from internal defects.

Room-temperature absorption spectra for a series of PbSe QDs are shown in Figure 2.4. Three distinct and sharp features are observed in most samples. As expected from quantum confinement, the onset of absorption is shifted substantially to the blue of the bulk band gap of 0.28 eV, with the 3-nm particles having a shift of 0.8 eV. From the absorption spectra we estimate a size variation of 5 - 10% which is consistent with the STEM results. The electronic structure of PbSe QDs was calculated by Kang,¹⁵ and we apply that formalism to the colloidal PbSe QDs. A calculation of the dipole-allowed optical transitions for ~8 nm PbSe QDs is shown in Figure 2.5. The calculation is based on a bulk $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian with all parameters determined by experiment, and accounts for the correct symmetry of the band-edge Bloch functions. The predictions of this calculation agree very well with the first and third transition peaks in the measured absorption spectra, although a systematic deviation between predicted and measured energies occurs for diameters <5 nm.¹⁸ However, the second peak, which has substantial oscillator strength, is not accounted for by Kang's theory. This situation was encountered in the study of PbS and PbSe QDs in glass. Two possible origins of the second peak have been proposed. The first is that the peak is the result of $1P_h - 1S_e$ and $1S_h - 1P_e$ transitions, which are formally parity-forbidden.


Figure 2.4: Linear absorption spectra of PbSe QDs ranging in diameter from 3 to 8 nm.



Figure 2.5: Linear absorption spectrum of ~8 nm PbSe QDs with theoretical calculations¹⁵ of the allowed one-photon transitions (gray bars). The location of parity-forbidden transitions among the states found by Kang are indicated (dashed arrows) as are the new states arising from the inclusion of the anisotropy of the bulk band structure (solid arrows).²²

Softening of the parity selection rule would allow new transitions among the states found by Kang's calculations. Another possible explanation is that the anisotropy of the bulk band structure produces new states not found by Kang.²² Analysis of the transitions that we observe in colloidal PbSe QDs does not allow a decisive assignment of the second absorption peak. However, the observed transition energies seem to favor the explanation based on the occurrence of parity-forbidden transitions among the states identified by Kang (see Figure 2.5).

Room-temperature photoluminescence from the PbSe QDs is bright and dominated by band edge recombination as suggested by the small Stokes shifts (40 - 90 meV) in Figure 2.6. The spectral bandwidth of the luminescence is comparable to that of the absorption peaks, which suggests that the bandwidth is a consequence of the particle-size distribution. We do not believe that the small structures observed just below 1400 nm are intrinsic to the nanocrystals. Luminescence from deep traps, typically observed as weak, broad, and highly Stokes-shifted emission, was never observed. Photoluminescence quantum yields at room temperature ranged between 12 and 81%. It is significant that no inorganic surface passivation, such as capping with a semiconductor shell,²⁴⁻²⁶ was required to obtain these quantum efficiencies as high as 81%. The large variation in photoluminescence quantum yield could be caused by differences in the surface reconstruction due to when the reaction was terminated. For instance, in CdSe QDs, the photoluminescence quantum yield shows a significant variation over the course of the synthesis, due to differences in optimal surface reconstruction during QD growth.²⁷



Figure 2.6: Band edge luminescence from PbSe QDs excited at (bottom to top) 740 nm, 990 nm, and 990 nm. The measured quantum yields ranged from 12 to 81%.



Figure 2.7: Luminescence decay for 3-nm PbSe QDs and a single exponential fit to the data (250-ns time constant). The instrument response to the excitation pulse is much shorter than the measured decay (1.1 ns FWHM).

Fluorescence decays were recorded at the peak emission wavelength for each sample. A typical decay is show in Figure 2.7, and exhibits a time constant of 250 ns. There is a trend of increasing decay time with increasing QD size; for the samples shown in Figure 2.6 the lifetimes are 250 ± 10 ns, 330 ± 10 ns, and 360 ± 60 ns. The observed decay times are longer than expected for a dipole transition, but shorter than expected for trap-related emission. In any case, the high quantum yields and small Stokes shifts argue against emission from traps contributing significantly to the observed spectra. A straightforward calculation of the transition dipole of the lowest exciton in PbSe QDs yields a radiative lifetime on the order of nanoseconds. Dielectric screening would be expected to increase the lifetime, by as much as two orders of magnitude if the bulk dielectric constants of PbSe are assumed. However, it is not clear that the bulk material parameters are relevant to the description of the nanocrystals. More work is needed to resolve this issue, which will have major implications for the use of PbSe QDs in applications.²⁸

2.4 Conclusions

In conclusion, we find that colloidal PbSe QDs synthesized following the procedure of Murray *et al.* exhibit excellent properties. These structures are comparable in quality to the best II-VI and III-V nanocrystals. They can be made very monodisperse and offer high photoluminescence quantum yields. As is the case with lead-salt QDs in glass hosts, not all of the observed optical transitions are understood. In addition, unexpectedly slow luminescence decays are observed. Work is in progress to address these issues.

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Chapter 3 The assignment of the second optical transition

Electronic structure calculations of lead-salt quantum dots have been successful in providing accurate energies of higher exciton states as well as the lowest exciton, electron and hole wavefunctions with the correct symmetries, as well as the interband dipole transition strengths and selection rules.¹⁴ Despite these successes, all current theories fail to explain the presence of additional structure in the optical absorption spectrum. We re-examine the leading explanations for these features in light of recent experimental results and then consider a new possibility, electric quadrupole transitions.

3.1 Introduction

The 4-band envelope function method of Kang *et al.* was the first treatment of Pb-salt quantum dots to provide accurate energies of higher exciton states as well as the lowest exciton, electron and hole wavefunctions with the correct symmetries, as well as the interband dipole transition strengths and selection rules.¹ However, as progress in the synthesis of Pb-salt nanocrystals lead to samples with narrower size distributions and hence, sharper exciton features, the presence of additional structure in the absorption spectrum was discovered.⁵⁻⁷ These unexplained absorption peaks appear between the first (1S – 1S) and second (1P – 1P) and the second (1P – 1P) and third (1D – 1D) dipole-allowed interband transitions and match the energy of dipole-forbidden transitions (1S – 1P and 1P – 1D).



Figure 3.1: Room temperature linear absorption spectra of PbSe QDs in tetrachloroethylene⁷ and PbS QDs in glass⁵. The bars indicate the strength of the dipole-allowed transitions calculated in the 4-band envelope function formalism (normal labels).¹ The dashed arrows indicate the predicted energies of the two lowest dipole-forbidden transitions (italicized labels).

3.2 **Prior work**

One experimental test of whether the true eigenstates of the QD are simultaneously parity eigenstates is to compare the one and two-photon absorption spectra.^{8, 9} If the QD wavefunctions are states of definite parity, then the transitions observed in the one and two-photon absorption spectra should be mutually exclusive: the one-photon spectra will connect states of different parity whereas the two-photon spectra will connect states of the same parity.

Kang proceeded to measure two-photon absorption spectra of PbS quantum dots using a standard pump-probe technique.¹⁰ The data fail to show the expected peak at the energy of the two-photon allowed 1P - 1 D resonance (the 1S - 1P resonance is outside the spectral range that could be covered in the experiment) and instead shows two strong resonances that are most likely due to the two-photon forbidden 1P - 1P and 1D - 1D transitions. These observations in the two-photon absorption spectra, when taken in conjunction with one-photon spectra shown previously, indicate a failure to obey parity selection rules.

Since the Pb-salt QDs have the rock-salt crystal structure and are inversion symmetric, intrinsic mechanisms for the parity-breaking such as the internal dipole field arising from the wurtzite crystal structure of CdSe and CdS QDs are ruled out. Instead extrinsic effects, like surface defects or non-symmetric shape or morphology were suspected to play a role. According to one estimate, these effects could result in a strong mixing of the parity eigenstates.¹⁰

Andreev *et al.* offered another mechanism to explain the additional structure in the Pb-salt QD's absorption spectrum. Working in the same 4-band envelope function formalism, they fully included the anisotropy of the bulk band structures of PbS and PbSe.² The effects on the QD electronic states were two-fold: (1) the isotropic states are split and their energies are shifted and (2) the resulting anisotropic states are a linear superposition of different isotropic states. This leads to several new parity-allowed transitions between the anisotropy-modified electronic states.

When applied to a 8-nm diameter PbSe QD in a phosphate glass host, Andreev *et al.* find good agreement between the unexplained peaks in the measured absorption spectrum and their calculations. Therefore, they claim that the inclusion of the anisotropy in the electronic structure calculations accounts for all the features in the linear absorption spectrum. However, absorption measurements of other Pb-salt QD samples conducted in our laboratory fail to reflect such agreement with the anisotropic electronic structure calculations. We pursued additional measurements to evaluate these two possible explanations.

3.3 Parity-forbidden transitions between isotropic states versus parity-allowed transitions between anisotropy-induced states

Room-temperature linear absorption measurements were conducted on a range of PbSe QDs sizes from a variety of different syntheses. Three different sources were used for colloidal samples from the synthesis detailed in Chapter 2.^{7, 11} PbSe QDs embedded in a phosphate glass host, the same synthesis as the



Figure 3.2: The energy of the several lowest optical transitions in PbSe QDs^{6, 7, 11} as determined from room-temperature linear absorption spectra. The scaling of the axes is described in the text. The horizontal lines indicate the predicted energies of dipole-allowed transitions and dipole forbidden transitions within the isotropic model¹ along with parity-allowed transitions within the anisotropic model.²

PbSe QDs used by Andreev *et al.*, were also examined.⁶ The positions of the lowest several absorption peaks were determined. In all samples, the first and second peaks were visible and when the sample quality was good enough (narrow enough size distribution), the third peak was also recorded.

Our findings are summarized in Figure 2. On the vertical axis, we plot the confinement energy of the Nth exciton state scaled by that of the lowest exciton and on the horizontal axis, the confinement energy of the lowest exciton state (essentially the QD size). Representing the data in this manner collapses the same transitions from different QDs sizes onto a horizontal line. The energies of the allowed electronic transitions predicted by the isotropic and the anisotropic models are shown. In addition, we calculate the position of the parity-forbidden transitions using the energies of the electron and hole states from the isotropic model.

We find that an explanation of the second absorption peak in terms of transitions between anisotropy-induced states significantly overestimates the energy. In fact, the energy of the second transition in the anisotropy model approaches that of the 1P - 1P dipole-allowed transition from Kang's original work.¹ On the other hand, the description of the second peak as a parity-forbidden 1S - 1P transition quite accurately reproduces the energy of the feature for nearly all of the samples studied.

Other experiments have yielded results that contradict the predictions of the anisotropic electronic structure calculations. Wehrenberg *et al.* studied the optical bleaching of PbSe NCs caused by direct electron injection into the QDs.¹² These measurements were sensitive to both interband (electron-hole) and intraband (electron-electron and hole-hole) transitions. The authors confirmed the $S_{e (h)} - P_{h (e)}$ interband transition and also observed $S_{e (h)} - P_{e (h)}$

intraband transitions. However, they did not observe the features predicted to only occur within the anisotropic model (for instance, the h3,h4 – e1,e2 interband transition, following the notation of Andreev *et al.*¹³). We take these results as further evidence supporting the assignment of the second peak as a parity-forbidden transition and not as a transition between anisotropy-induced states.

However, recent electronic structure calculations of PbSe nanocrystals (NCs) using tight-binding methods have called the explanation of the second absorption peak in terms of parity-forbidden transitions into question. Although Allan *et al.* did find that consideration of NCs with more complex shapes and less symmetries slightly relaxes the parity selection rule, they were never able to reproduce the experimentally observed oscillator strength of the second absorption peak.⁴ Obviously, this argues against Kang's hypothesis that strong parity eigenstate mixing results from the break-down of inversion symmetry at the QD surface.¹⁰

Although the mechanism remains in question, the experimental evidence still strongly supports the assignment of the second absorption peak as a S – P interband transition. In fact, our recent measurements that time-resolved the excited state relaxation of electrons and holes in PbSe QDs showed that the first and second transitions share a common state, $1S_{e}$ (h). Therefore, we consider another possible explanation for the second absorption peak that does not violate the parity selection rule, an electric quadrupole transition.

3.4 Quadrupole transitions

The interaction between a quantum dot and an optical field may be described semi-classically by use of a multipolar expansion of the interaction Hamiltonian.¹⁴ For far-field excitation the first term in this expansion, the electric dipole term, gives rise to a response that is considerably stronger than that produced by subsequent terms. This is because the physical dimension of the QD is much smaller than the wavelength of the light and also because of the weak spatial variation of the field.

It has been shown by Zurita-Sanchez *et al.* that in cases where the spatial variation of the optical fields is much stronger, as is the case in near-field excitation, the higher terms in the multipolar expansion cannot be ignored.¹⁴ For instance the next higher terms, the electric quadrupole and magnetic dipole, respond to the gradient of the electric field. Thus, in cases of large field gradients, the optical absorption spectrum is modified by the inclusion of electric quadrupole transitions of strength comparable to the electric dipole transitions. However all of the experimental situations under which the extra absorption features have been observed employed plane-wave optical excitation. The quadrupole response to this applied field should be negligible when compared to the electric dipole response.

The calculations by Zurita-Sanchez *et al.* are specific to a semiconductor QD with hole wavefunctions expanded in p-like basis states and electron wavefunctions expanded in s-like basis states, like II-VI and III-V materials.¹⁴ However for Pb-salt QDs, both electrons and holes are expanded in the same set of basis states. This leads to additional terms in the interband matrix elements that are not present in II-VI and III-V semiconductor QDs.¹ We

considered the possibility of an unique and large contribution to the quadrupole transition moment in IV-VI QDs that could compensate for the small field gradient of the applied electric field.

We analytically evaluated the quadrupole moment for PbSe QDs (see Appendix). The magnetic dipole moment has been ignored; generation of the necessarily large magnetic field srengths requires the use of an azimuthally-polarized optical near-field.¹⁵ Although not all of the necessary parameters are available from $\mathbf{k} \cdot \mathbf{p}$ theory, we numerically estimate the order of magnitude of the quadrupole moment and find it is smaller than the dipole moments by a factor of approximately the wavelength of light squared. Therefore, it appears that the only way to have an electric quadrupole transition of strength comparable to an electric dipole transition is with application of a large field gradient. However, might it be possible that the applied plane-wave excitation develops a substantial gradient in the vicinity of the QD due to dielectric effects? This is our next consideration.

The dielectric theory of nanostructures is a current and important topic of theoretical and experimental studies. It was shown experimentally using electrostatic force microscopy that the static dielectric constant of a single CdSe NC is uniform and consistent with the value of the bulk semiconductor.¹⁶ Recent calculations by Delerue *et al.* have shown that, with the exception of a surface layer with a thickness on the order of the interatomic spacing, the bulk value of the semiconductor dielectric function is recovered inside the nanoparticle.¹⁷ Given these results, it is reasonable to model the dielectric response of the QD as a solid sphere of the bulk dielectric constant ε_2 . Let this sphere then be immersed in background dielectric ε_1 ($\varepsilon_2 > \varepsilon_1$) that contains an initially uniform electric field.

This problem is one solved in basic electrostatics.¹⁸ Outside, the initially uniform field is distorted by the presence of the dielectric sphere. Inside the sphere, the field remains uniform although its magnitude is reduced by a local field factor,

$$F = \frac{3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} \tag{3.1}$$

Therefore, this simple model illustrates the lack of an electric field gradient in the interior region of the QD. However, in light of Delerue's calculations, we should expect a field gradient at the surface. Let us estimate its magnitude, $|\Delta E / \Delta z|$.

Given their large dielectric constants ($\varepsilon(\infty) = 18$ for PbS, 22 for PbSe¹⁹) the dielectric screening is very strong for the Pb-salts. For instance, a PbSe sphere immersed in air has a local field factor, F ~ 1/8. Therefore, the internal field is reduced to about 10% of the magnitude of the externally applied electric field. In addition, this reduction in the field strength occurs on a length scale of atomic dimensions, say approximately the lattice constant. Therefore,

$$\left|\frac{\Delta E}{\Delta z}\right| \approx \frac{0.9E_0}{0.6 \text{ nm}} \approx 1.5 \frac{E_0}{\text{nm}}$$
(3.2)

For comparison, the estimated electric field gradient from the optical near-field excitation scheme described by Zurita-Sanchez is ~ $0.5 E_0 / nm.^{14}$

Yet, it is difficult to explain how electrons delocalized in the core of the QD could couple effectively to this gradient existing at the surface. However, it is possible that surface localized electrons or holes would couple exceptionally-well to this field gradient. The intrinsic gap states proposed by Sercel *et al.*

would be one such possibility.²⁰ Experiments are currently underway to address the role of these and other dielectric effects on the optical and electronic properties of the Pb-salt QDs.

3.5 Conclusions

We have reviewed the prior explanations for the unexplained structure observed in the absorption spectra of high-quality Pb-salt QDs. It was shown that the energy positions of these absorption peaks are better explained by the parity-forbidden transitions between isotropic electronic states rather than parity-allowed transitions between anisotropic electronic states. It was suggested that deviations from inversion symmetry near the nanocrystal surface were responsible for the parity-breaking. Recent atomistic electronic structure calculations have called this hypothesis into question; the predicted strength of the parity-forbidden transitions is always much weaker than that observed in experiment.

As one possible explanation, we have considered the role of electric quadrupole transitions. Under conditions of large applied electric field gradients, quadrupole transitions have been shown to modify the optical absorption spectrum. While the measurements revealing the unexplained absorption structure were conducting using far-field optical excitation, we propose that the strong dielectric screening experienced by the Pb-salt QDs could generate a surface-localized electric field gradient comparable in magnitude to that obtained in near-field experiments. Experiments are currently underway to address the role of these dielectric effects on the properties of lead-salt QDs.

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Chapter 4 Photoluminescence studies of lead-salt nanocrystals

4.1 Introduction

Lead-salt quantum dots (QDs) are among the few materials that can provide size-quantized electronic transitions at technologically-important infrared wavelengths. Structures containing these QDs may find use in optoelectronic applications as well as in biophysical applications such as fluorescence microscopy. Beyond the initial characterization studies, such as those presented in Chapter 2, work on the emission properties of these QDs has concentrated on application-related aspects.^{1, 2} However, there is a lack of understanding of the emission characteristics of PbSe QDs.

For instance, the 50 to 100 meV Stokes shift observed in global photoluminescence (PL) measurements, while not interpreted directly in terms of the homogeneous spectrum and intrinsic nanocrystal properties, does nevertheless, suggest a Stokes shift in the single-particle spectrum.³ This may arise from the vibronic nature of the transitions. Although the coupling of excitons to optical phonons is expected to be very weak in PbSe, phonon-assisted transitions may be strong due to non-Franck-Condon effects.⁴

In addition, the observed photoluminescence decay times are longer than expected for a dipole transition. A straightforward calculation of the transition dipole of the lowest exciton in PbSe QDs yields a radiative lifetime on the order of nanoseconds. Dielectric screening would be expected to increase the lifetime by as much as two orders of magnitude if the bulk dielectric constants of PbSe are assumed. However, recent measurements that tested this simplistic dielectric screening hypothesis by the systematic variation of the host dielectric constant appear not to follow the proper trend.⁵ More generally, it is also surprising that the luminescence properties of QDs can be explained in terms of only intrinsic volume states when a large portion of the atoms comprising a QD lie at the surface. In fact, recent far-infrared absorption measurements of PbSe QDs reproducibly observed the presence of mysterious high-frequency absorptions that cannot be explained by treating the QD as truncated crystalline lattice.⁶

The topic of fine structure in the energy spectra of QDs has been a subject of much interest and has been invoked to explain the shift between absorption and emission peaks as well as the observation of long radiative lifetimes in CdSe.^{7,8} Kang's envelope function calculations of the electronic structure of the IV-VI QDs did include these many-body perturbations. Their effects are as follows: the Coulomb interaction does not split the lowest transition and the exchange interaction is small (10 meV in comparison to ~ 1 eV transition energy).⁹ Still, other effects that are expected to influence the electronic spectra cannot be included in envelope function methods. Features like the multivalley nature of the IV-VI semiconductors and the influence of the surfaces (surface molecules or surface reconstruction) have been addressed with tight-binding theories.¹⁰⁻¹²

Here, we report studies of the band-edge electronic structure of PbSe and PbS QDs using PL spectroscopies. We observe, for the first time, a splitting in the PL spectrum that is also consistent with a calculation of the splitting from intervalley coupling. Size-selective PL measurements reveal broad emission lines even when the inhomogeneous broadening effects of the size distribution are eliminated suggesting that the degeneracies arising from the different valleys are also split by other mechanisms. We also observe that the surfaces do impact some of the emission properties and we consider explanations for all for all of these features.

4.2 Sample preparation and initial characterization

High-quality colloidal PbSe and PbS NCs were synthesized as reported previously in the literature. To perform temperature-dependent measurements, an optically transparent low-temperature host is required. Several suitable low-temperature glass formers, typically used in the visible region of the electromagnetic spectrum, were reviewed; however, all of these compounds have absorptions in the infrared. For instance, 2,2,4,4,6,6,8-heptamethylnonane (HMN) absorbs for wavelengths > 1500 nm, precluding optical measurements of larger QDs in this host.

To circumvent this problem with low-temperature hosts, we fabricated solid-state films by drop-casting the QDs from hexane onto a glass coverslip. Visual inspection reveals light and dark regions, indicating that the films do not layer uniformly. This is expected; the hydrophobic QDs should cluster on hydrophilic glass surface, leading to many separated domains on the surface.¹³ However, the optical measurements probe large regions of the sample and therefore average over the different domains. Room-temperature absorption and photoluminescence spectra were measured immediately after the films were prepared and their spectral features did not change in the span of several weeks over which our experiments were conducted.



Figure 4.1: Comparison of the absorption and PL spectra in solid state film samples and colloidal samples. The solid state film absorption has been corrected for scatter by subtracting a $1/l^4$ background. The peak in film absorption at ~ 0.9 eV is from oleic acid.

The samples were loaded into a Helium vapor cryostat and cooled to temperatures as low as 15 K. The PL was excited with the spectrally-resolved emission from a tungsten-halogen lamp or one of several narrow-band laser sources: a home-built continuous-wave Ti:sapphire laser (775 - 930 nm), a commercial grating-tuned diode laser (1520 – 1570 nm), and a fixed wavelength diode laser (~ 980 nm). The emitted light was collected at right angle to the excitation, spectrally-resolved by a 0.2-meter monochromator, and detected with a TE-cooled extended InGaAs photodiode. The spectral resolution of the system was typically less than 5 meV.

Room-temperature optical absorption spectra of the solid state films reveals the same excitonic structure as in the colloids from which they were made although superimposed on a scattering background (Figure 4.1). The PL from the films is still dominated by band-edge emission although we consistently find that the emission spectra are red-shifted and narrower than that from the colloids. Transmission electron micrographs of similar film assemblies of PbSe QD show nearly close-packed ordering within a given domain, likely separated by the surface ligands (oleic acid ~ 2 – 3 nm, head-to-tail).³ Given these features in the structural characterization, we tentatively attribute the narrowing and red-shifting of the emission spectra to electronic energy transfer (EET) between the NCs.

EET is a one-step process in which energy is simultaneously transferred from an excited species (donor) to an unexcited species (acceptor). In this way, it is distinct from radiative transfer in which an intermediate photon is first emitted by the donor and then absorbed by the acceptor. EET has been previously observed in close-packed arrays of CdSe QDs¹⁴ but this is its first observation with PbSe NCs. Work is currently underway to address this topic in more detail. In the remainder of this work, we consider EET as only a mechanism that reduces the inhomogeneous broadening effects of the QD size distribution on the emission spectra.

4.3 Global photoluminescence measurements

Figure 4.2 shows the change in the PL spectrum with temperature for a solid state film of 3.7-nm PbSe NCs. It is important to note that that the excitation photon energy is well above the energy of the lowest transition. In this case, all of the QDs in the sample, regardless of their size, are excited and contribute to the ensemble emission spectrum. This is referred to as global excitation. Figure 4.2 confirms that the resulting PL spectrum is broad and comparable to the width of the absorption peaks (see for example, Figure 1) suggesting that the bandwidth is a consequence of the particle-size distribution.

As the temperature decreases, the peak energy of the emission spectrum shifts to lower energy. However, in films of smaller QDs, the peak barely shifts at all. These observations are consistent with the size-dependent temperature variation of the lowest transition of PbSe QDs by Olkovets *et al.*¹⁵ We also observe that the shape of the low-temperature PL spectrum is different than the spectrum measured at room temperature.

To investigate whether this structure in the PL spectrum might be due to sample preparation, we also performed low-temperature PL measurements on colloidal samples in HMN. Figure 4.3 shows the low-temperature emission spectra for PbS QDs in colloidal and solid state film preparations. Although the strength of the two PL features located at approximately 0.97 eV and



Figure 4.2: The peak of the PL spectrum shifts to lower energy and narrows with decreasing temperature. The excitation energy is 1.1 eV. The feature observed in all of the traces at 0.9 eV is an artifact of the grating.



Figure 4.3: Comparison of the low-temperature PL spectra from PbS solid state films and colloidal samples at an excitation energy of 1.27 eV. The energy position of the PL structure (~ 0.97 eV and ~ 1.15 eV) does not change with sample preparation, although the strength of these features does.

1.1 eV does change with sample preparation, it is important to note that their position does not.

Additionally, we measured the intensity dependence of the emission spectrum by using continuous-wave and pulse laser excitation. Typically, the emission resulting from carriers trapped at surface sites exhibits a different intensity dependence than the emission from the intrinsic core states of the QD.¹⁶ We find that PL spectrum maintains its shape even as the peak intensity of the excitation light is varied by a factor of ~ 10^{10} (Figure 4.4). We take both of these observations as experimental evidence that the structure in the PL spectrum is not solely an extrinsic surface effect.

Figure 4.5 displays the PL spectra measured at 15 K for 3 different sizes of PbSe QDs. A clearly-discernable second peak is observed on the low-energy side in the small PbSe sample. Although the larger-sized PbSe QDs exhibit no obvious second peak, their PL spectra are asymmetric with a tail extending on the low-energy side. Also shown in Figure 4.5, is the systematic decomposition of each of these PL spectra into a sum of two Gaussians. For smaller sized QDs, we find that the width of the Gaussians and also their separation is larger. The separation between the peaks varies from ~ 20 meV to 130 meV as the PbSe QD size decreases from 4.6 nm to 3.2 nm. A 2-nm diameter PbS QD (not shown here) exhibits a peak separation of ~ 310 meV.

4.4 Size-selective photoluminescence measurements

In the measurements presented so far, the widths of the emission peaks were reflective of the size distribution rather than any intrinsic NC properties. One



Figure 4.4: The intensity dependence of the PL spectra was explored using CW and pulsed excitation. The measured spectra are nearly identical despite a difference in peak intensity of approximately 10¹⁰. Based on this observation, we rule out contributions from surface states.



Figure 4.5: PL spectra from PbSe QD solid state films at T = 15 K. The dashed curves are the measured PL spectra and the solid curves are the best-fit two-Gaussian decomposition of the measured spectra.

way to circumvent this inhomogeneous broadening effect on the emission spectra is to utilize size-selective excitation. In contrast to the global excitation experiments discussed above, a narrow-band excitation source with a photon energy tuned within the low-energy tail of the QD absorption spectrum is used to photo-excite only the largest QDs within the sample. Subsequently, only this subset of the largest QDs contributes to the line-narrowed emission spectrum. Based on the availability of laser sources in our laboratory, we measured line-narrowed emission from one sample. The results are shown in Figure 4.6 for a 4.7-nm PbSe QD.

Compared to the globally-excited emission, the bandwidth of the features observed using size-selective excitation is narrower. However, the bandwidth is still broader than that observed for CdSe QDs in either size-selective PL (1 – 10 meV) ¹⁷ or single-dot PL (< 1 meV) experiments.¹⁸ Another interesting feature is the appearance of strongly anti-Stokes shifted (A-S) PL in the case of the reddest excitation (0.790 eV).

4.5 Discussion

One possible explanation of the splitting observed in the PL spectra involves the degeneracy splitting of the lowest transition via the coupling of equivalent L-valleys. Allan *et al.* have performed a calculation of the intervalley splitting and show it to be effectively large.¹² In Figure 4.7, the maximum energy splitting from this calculation is compared to the measured energy separation of the two PL features obtained from the Gaussian decomposition of the global PL spectra over a range of temperatures. The calculation and measurements agree quantitatively over the range of sizes studied here.



Figure 4.6: Line-narrowed PL from 4.7-nm PbSe at T = 15 K. The first absorption peak (not shown) is at 0.95 eV. The size-selective excitation is tunable between 0.816 and 0.790 eV. The solid lines labeled with markers represent the line-narrowed emission spectra. The solid black like is the globally-excited PL spectrum and the dashed lines show the best-fit two Gaussian decomposition of the global PL spectrum from Figure 4.5.


Figure 4.7: The experimentally measured PL feature splitting for three different PbSe QD sizes. The splitting is found to increase with both decreasing temperature and size. We compare these measurements to maximum splitting predicted in calculations by Allan *et al.*

Another mechanism we are currently pursuing to explain the PL splitting involves the role of the intrinsic gap states proposed by Sercel *et al.*²⁰ Though we lack a quantitative understanding of these states in PbSe at the moment, qualitatively, these gap states are predicted to play an increasing role in small QDs. For instance, transitions between the gap states and the conduction band could determine the absorption band edge in the smallest QDs.²⁰

The explanation for the broad emission lines observed in size-selective excitation experiments is likely the result of additional degeneracy splittings. The lowest transition will be composed of 64 lines which are shifted by different effects: Coulomb interaction, exchange interaction, inter-valley couplings and shape asymmetry effects.^{12, 19}

The A-S PL is difficult to explain. The presence of a decaying A-S tail in PL has been observed previously at room-temperature. It was explained by models involving surface states in energetic proximity to the intrinsic QD core state, and the energy up-conversion occurred by phonon absorption.²¹ Generally, it is a feature of II-VI and III-V semiconductor QDs for surface ligands and surface reconstruction to have a major influence on the band-edge electronic states and optical properties.^{11, 22}

However, it is difficult to explain the strongly-peaked A-S PL (~ 10 meV) in the case of PbSe. Though this energy is the same order of magnitude as the phonon energy in PbSe (~ 17 meV), these vibrational modes should not be populated at low temperature. Additionally, PbSe appears to be more resistant to the deleterious surface effects like dangling bonds. Atomistic calculations have found that PbSe, because of its large ionicity, does not require special care to saturate dangling bonds and remove surface states from

the energy gap.¹⁰ This may also explain the high PL efficiency in PbSe QDs and also why no trapped states have been observed experimentally.¹²

4.6 Conclusions

In conclusion, we report photoluminescence (PL) studies of the band-edge electronic structure of PbSe and PbS QDs using PL spectroscopies. We observe, for the first time, a splitting in the emission spectrum. The splitting increases as the QD size is decreased and is also approximately a factor of two larger in PbS than in PbSe. The magnitude of this splitting and its variation with QD size is consistent with a calculation of the splitting of the lowest transition due to the coupling of equivalent L-valleys. The role of intrinsic gap states could be another way to explain the splitting in the PL spectra. Sizeselective PL measurements reveal broad emission lines even when the inhomogeneous broadening effects of the size distribution are eliminated. This suggests that the energy level degeneracies are also split by other mechanisms including the Coulomb interaction, exchange interaction, and shape asymmetry effects. We also find that the surfaces do impact the strength of the emission features but not their energies. This is, perhaps, a reflection of the robustness of PbSe QDs against the formation of surface states.

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Chapter 5 Time-Resolved Intraband Relaxation of Strongly-Confined Electrons and Holes in Colloidal PbSe Nanocrystals

The relaxation of strongly-confined electrons and holes between 1P and 1S levels in colloidal PbSe nanocrystals has been time-resolved using femtosecond transient absorption spectroscopy. In contrast to II-VI and III-V semiconductor nanocrystals, both electrons and holes are strongly confined in PbSe nanocrystals. Despite the large electron and hole energy level spacings (at least 12 times the optical phonon energy), we consistently observe picosecond time scale carrier relaxation. Existing theories of carrier relaxation cannot account for these experimental results. Mechanisms that could possibly circumvent the phonon bottleneck in IV-VI quantum dots are discussed.

5.1 Introduction

A dramatic reduction in the relaxation rate of carriers in three dimensionallyconfined quantum systems is predicted to occur if the energy-level spacing is several times greater than the phonon energy.^{1, 2} While an interesting scientific issue in nanocrystal physics, this "phonon bottleneck" would also have major implications for applications of quantum dots (QDs). In a QD gain medium, for instance, excited carriers should rapidly relax non-radiatively to their lowest states before the emission of a photon. In prior experiments on colloidal QDs, ultrafast intraband carrier relaxation has been observed and a mechanism explaining the process has been widely adopted. This "Auger-like" electron-hole scattering process, described by Efros *et al.*, relies on the high density of hole states in II-VI and III-V semiconductor QDs plus the assumption of fast hole relaxation via phonon emission.³ In this case, electron relaxation occurs by coupling to the large density of hole states and happens on a picosecond to sub-picosecond time scale. The strongest evidence in support of the Auger-like process comes from experiments in which this mechanism is intentionally obstructed. When the electron is forced to relax in the absence of a spectator hole, an increase of an order-of-magnitude in the relaxation occurs without the Auger-like mechanism.

QDs of the IV-VI semiconductors PbS, PbSe, and PbTe differ substantially from their II-VI and III-V counterparts. With large electron and hole Bohr radii (for example, in PbSe: a_{er} = 23 nm, a_h = 24 nm), both electrons *and* holes are strongly confined. This leads to simple and sparse energy spectra for IV-VI QDs.⁷ Such materials should be ideal for studying electron dynamics in a system with energy levels spaced more than a phonon-energy apart. In contrast, the electron is confined only in small II-VI and III-V QDs, and the hole is *never* strongly confined (for example, in CdSe: $a_e = 3$ nm, $a_h = 1$ nm). In addition, the confinement-induced coupling between the three (heavy-hole, light-hole, and split-off) valence bands further complicates the already dense ladder of hole states and leads to congested energy spectra in II-VI and III-VI QDs. Intraband electron relaxation in II-VI and III-V nanocrystals⁴⁶ is dominated by processes that cannot occur in IV-VI materials, so studies of electron relaxation in II-VI and III-V nanocrystals do not provide direct information about the relevant processes in IV-VI structures.

A consequence of the sparse spectra of IV-VI QDs is that carrier relaxation *via* the Auger-like process should be impossible. Therefore, it is surprising that prior studies of IV-VI QDs did not observe a phonon bottleneck.^{8, 9} Here, we report the first experiments to directly time-resolve the intraband electron and hole relaxation in strongly-confined colloidal PbSe nanocrystals.¹⁰ At low photo-excited carrier density, the 1P to 1S relaxation time is observed to increase from 3 to 9 ps as the QD diameter increases from 4.3 to 6.0 nm. At high carrier density, the relaxation time ranges between 2 and 3 ps. In cases where carriers are pumped into higher excited states, we observe a relaxation time of ~3 ps, independent of the carrier density. No known mechanism accounts for these fast relaxations, and some possibilities are discussed.

5.2 Experiment

High-quality colloidal PbSe NCs were synthesized as reported previously in the literature^{11, 12}. A colloidal silica host was developed and the PbSe QDs were dispersed into the matrix¹³. The resulting solid films were 240-µm thick and contained approximately 0.1% volume occupancy of QDs. Optical characterization of the films reveals excitonic structure in the absorption and emission spectra, as well as photoluminescence lifetimes comparable to those of the colloids (Figure 5.1).

The electronic structure of PbSe and PbS NCs was calculated by Kang *et al.* using a 4-band envelope function formalism.¹⁴ The first 2 electron and 2 hole



Figure 5.1: The absorption (solid line) and photoluminescence (shaded region) spectra for 6-nm PbSe QDs in the colloidal silica film. The lowest few electronic states are calculated using a 4-band envelope function formalism (inset). The strength of the lowest dipole-allowed transitions are indicated by vertical lines. The second absorption feature (italicized label) is discussed in the text. Separate control measurements of a blank film show that the absorption peak near 0.6 eV is due to the host.

states and the lowest dipole-allowed transitions for a 6-nm diameter PbSe QD are shown in Figure 5.1. The states are labeled by total angular momentum (j) and parity (π) but for simplicity, we adopt the usual nomenclature and refer to the states according to the angular momentum of the envelope function $(\ell = 0, 1... \text{ as S}, P,...)$. To date, electronic-structure calculations of Pb-salt QDs fail to reproduce the second absorption peak and some attention has been paid to this previously^{14,9, 15-18}. The energy of this peak matches that of the dipole-forbidden transitions between $1S_{e(h)}$ and $1P_{h(e)}$ states. However, Allan et al. did not find significant strength for these transitions even when considering asymmetric QDs in their tight-binding calculations¹⁸. Still, we are intrigued to find that our ultrafast measurements support the assignment of the second absorption peak to $1S_{e(h)}$ - $1P_{h(e)}$ transitions (see below). The nature of these unexplained transitions will be more fully addressed in a future work but in the remainder of this chapter, we will assume this peak arises from $1S_{e}$ $_{(h)}$ - 1P $_{h (e)}$ transitions. For the PbSe QD sizes studied here, the 1P $_{e (h)}$ to 1S $_{e (h)}$ energy spacing is between 200 and 300 meV.

The vibrational modes are also modified by confinement and in QDs of polar materials, the optical mode with $\ell = 0$ is expected to contribute most strongly to relaxation by phonon emission. As shown in recent experiments by Hyun *et al.*, this mode has an energy of approximately 17 meV over the range of QD sizes studied here¹⁹. Under these circumstances, a phonon bottleneck is expected because the $1P_{e (h)}$ - $1S_{e (h)}$ energy spacing is 12 to 18 phonon energies.

Two-color transient absorption experiments were performed to investigate the intraband carrier dynamics. In this experiment, a strong pump pulse incident on the sample generates excited electron-hole pairs. A weak, timedelayed probe pulse monitors the absorption of the lowest optical transition. In the limit that $\alpha L < 0.1$ (α is the linear absorption coefficient and L is the propagation length), the differential transmittance (DT) of the probe beam, $\Delta T/T_0 = (T-T_0)/T_0$, is directly proportional to the sum of the electron and hole populations. Here, T and T₀ are the probe beam transmission with and without the pump. The subsequent relaxation of the photo-excited carriers is observed by monitoring the DT as a function of the time delay between pump and probe pulses. We are unable to separate electron and hole contributions to the DT signal because of their similar electronic structures. Therefore, the mirror image transitions are always implied.

The pump and probe pulses were generated in identical optical parametric amplifiers (OPAs), simultaneously pumped by a Ti:sapphire regenerative amplifier. Each OPA was tunable in wavelength from 450 to 3000 nm. The pump and probe pulses were typically 100 fs in duration, and the time resolution of the measurement was better than 300 fs for all combinations of wavelengths employed in this work. The pump beam was mechanically chopped and the probe beam was split into signal and reference beams and measured in balanced detection using a lock-in amplifier. The probe beam was always set to the peak absorption wavelength of the lowest optical transition, $1S_e - 1S_h$, and two different cases were investigated. In case 1, the pump beam was tuned to the $1S_{e (h)} - 1P_{h (e)}$ transitions. In case 2, carriers were excited into much higher excited states by pumping with visible light ($\hbar \omega = 2.4 \text{ eV}$). The pump pulse energies were typically varied over the range of tens to hundreds of nanoJoules. All of the measurements presented here were conducted at room temperature.



Figure 5.2: Room-temperature population dynamics of the 1S states, for the indicated densities of photo-excited carriers. The pump pulse is resonant with the $1S_h - 1P_e$ transition. The mirror-image $1S_e - 1P_h$ transition is also pumped, but for clarity this is not shown on the energy-level diagram (inset). The expanded time scale (right panel) shows carriers entering 1S states. The dotted line is the instrument response.



Figure 5.3: The population dynamics of the $1S_e - 1S_h$ transition under $1S_{e\ (h)} - 1P_{h\ (e)}$ excitation, for different excitation levels. $\langle N_{e\cdot h} \rangle$ is the average number of photo-excited electron-hole pairs per QD. The time at which the population peaks is extracted from a fit to the data (solid lines). The traces are normalized and then offset for clarity. The delay stage step size was changed at 2 ps, giving the appearance of an abrupt change in noise level.

<u>1S - 1P Excitation</u>

Figure 5.2 shows a typical measurement when the pump photon energy is resonant with the $1S_{e (h)} - 1P_{h (e)}$ transitions. In the left panel, we observe the population of the 1S states increasing on the time scale of the pump pulse, and then decaying within 40 to 100 ps. To focus on carriers entering 1S states, we expand the time scale in the right panel.

The population of the 1S states exhibits two components, one rising within the time duration of the pump pulse and the other rising for several picoseconds thereafter. The energy-level diagram (Figure 5.2, inset) illustrates their origin: (1) the component rising with the pump pulse develops because the pumped and probed transitions share a state (in the case shown, $1S_h$); thus, one part of the transition is populated directly by the pump pulse, and (2) the slower rising component is caused by carriers undergoing intraband relaxation ($1P_e$ to $1S_e$ for the case shown). The first component supports our assignment of the second absorption peak to $1S_{e(h)} - 1P_{h(e)}$ transitions.

The magnitude of these signals also contains valuable information. We would expect the fast and slow-rising components to contribute equally to the total signal magnitude on the basis of the similar electronic structure. However, the measurements indicate that the 1S states are almost 7-times more likely to be populated by direct excitation than by the 1P to 1S relaxation. This observation suggests the presence of an alternate decay channel. However in what follows, we will focus on the 1P to 1S relaxation process.

Figure 5.3 shows the DT traces for the sample in Figure 5.2 over a wider range of carrier densities, but normalized to the peak DT. The curves are fit to



Figure 5.4: 1P - 1S relaxation time is plotted versus QD diameter.



Figure 5.5: Population dynamics of the $1S_e - 1S_h$ transition with photo-excited carrier density for a 2.4-eV pump.

extract the time at which the population of the 1S states peaks, and this is taken to be the 1P to 1S relaxation time. With an average of 0.5 electron-hole pairs per QD ($\langle N_{e-h} \rangle = 0.5$), the relaxation is observed to occur in 6 ps, and this time decreases as the photo-excited carrier density is increased. We observe this trend in all of the QDs studied. The fastest relaxation time observed is 2 ps, which is approximately 3 – 4 times larger than the electron relaxation time in bulk PbSe. We repeated these measurements on a range of QD sizes between 4.3 and 6.0 nm and find the 1P to 1S relaxation time increases with QD size (Figure 5.4). In these measurements the carrier density was kept low to avoid multi-carrier effects in the relaxation.

<u>High-energy excitation</u>

We also explored the effect of exciting carriers far above the 1P states. This has the advantage of not directly populating a state that is probed. Accordingly, the rise of the $1S_e - 1S_h$ population shown in Figure 5.5 now consists of a single component. When a 4.9-nm-diameter QD is pumped at 2.4 eV, we find that the $1S_e - 1S_h$ population develops in approximately 3 ps at both low ($<N_{e-h}> <1$) and high ($<N_{e-h}> = 10$) carrier densities. This insensitivity to carrier density is in contrast to the results obtained when exciting directly into 1P states. Therefore, we need to consider these two regimes separately.

5.3 Discussion

We now turn to a discussion of the possible relaxation mechanisms. One way to explain the intraband relaxation of carriers from states far above 1P (Figure 5.5) and the observed insensitivity to carrier density is impact ionization. In this process, an electron with energy in excess of twice the $1S_e - 1S_h$ energy

difference (ΔE_{1S-1S}) relaxes to its 1S state by exciting additional electrons from $1S_h$ to $1S_e$.²⁰ Thus, two or more cooled carriers may result from a single highlyexcited one. Schaller *et al.* have attributed the appearance of multi-exciton signatures in the population decay of the 1S states with $\langle N_{e-h} \rangle < 1$ to impact ionization.²¹ At low carrier density and high-energy excitation ($\hbar \omega$ =2.5* ΔE_{1S-1S}), we also observe a fast decay component from the 1S states. We do not observe this for 1S – 1P excitation.

The 1P to 1S relaxation requires a different explanation. Any possible role of multi-carrier effects is excluded by consideration of the relaxation for $\langle N_{e\cdot h} \rangle$ $\langle 1$. Yet even in this case, the observed relaxation time is between 3 and 9 ps, with the smallest QDs exhibiting faster relaxation. These results are in reasonable agreement with the upper bound on the intraband relaxation time set by Wehrenberg *et al.*⁹.

The contribution of multiphonon²² or polaron²³ effects in the relaxation are ruled out because they cannot account for efficient relaxation over such large energy level spacings. However, there may be additional states that could facilitate the relaxation. One possible source of such states is the four equivalent L-valleys of PbSe. Splitting of these degenerate states is calculated to be as large as ~100 meV in the smallest QDs.¹⁸ Even with such splitting, however, the energy gap between the 1P and 1S manifolds would be several phonon energies.²⁴

It is also possible that the surface could play a role in the relaxation that we observe. Darugar *et al.* have studied the relaxation from the lowest transition in CdSe QDs and quantum rods and find that QDs relax faster than quantum rods of the same diameter. Darugar *et al.* correlate this to the predicted change in excited electron density on the nanostructure surface, and conjecture that

coupling between the excited electrons and large surface molecules could lead to efficient carrier thermalization.²⁵

Before concluding, we note the similarity in intraband relaxation times (1) reported in this work for electrons and holes in PbSe QDs and (2) observed for electrons in II-VI and III-V semiconductor QDs when the Auger-like electron-hole scattering mechanism is intentionally obstructed.⁴⁻⁶ These results suggest the existence of a non-radiative relaxation channel on the 1 to 10 ps time scale that is accessible to strongly-confined electrons and/or holes in colloidal QDs, *independent of the material system*. This too suggests that the surface may be an integral part of the intraband relaxation mechanism. Renewed efforts to incorporate the surface's role into the relaxation may be needed.

5.4 Conclusions

In conclusion, we have time-resolved the relaxation of electrons and holes in colloidal PbSe NCs. In stark contrast to other semiconductor NCs, both electrons and holes are strongly confined in PbSe QDs. Therefore, Auger-like electron-hole scattering cannot be invoked to explain the intraband relaxation of charge carriers. In cases where carriers are pumped into higher excited states, we observe a relaxation time of ~3 ps, independent of the carrier density. We tentatively attribute this behavior to carrier cooling *via* impact ionization. When the P states are directly populated with, on average, less than one electron or hole per QD, the 1P to 1S relaxation time increases from 3 to 9 ps as the QD size is varied between 4.3 and 6.0-nm in diameter. The size dependence of this relaxation may be correlated with the change in electron density on the QD surface as previously suggested in the literature. This could

explain the similarity of the relaxation times observed in PbSe QDs and in surface-modified colloidal II-VI and III-V QDs. Known mechanisms based on interior electron states and vibrational modes cannot account for the experimental results, which suggests that surface atoms and ligands may play a major role.

5.5 Acknowledgements

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Chapter 6 Future directions

The difficulty in assessing the role of the surfaces on the electronic and optical properties of semiconductor quantum dots (QDs) remains a leading problem. A next logical step of the research would be to obtain information on the microscopic structure of the surface or defects by chemical or structural modification.

While techniques like electron microscopy and x-ray diffraction have been used to characterize the structure of the crystalline QD core, investigations of the surface shell have remained largely untouched. To establish the structure of the surface shell, nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) have been applied successfully. NMR, by virtue of its sensitivity to local chemical environments, has the capability of supplying information about the crystallite surface. For instance, Becerra *et al.* were able to determine that only Cd dangling bonds were successfully passivated in CdSe NCs.¹ XPS was later applied and yielded similar information about the surface passivation.² Both of these techniques would be useful in assessing the surface quality of PbSe and as a test of the assertion that PbSe QDs are less susceptible to the presence of gap states.³ In addition specific electronic structure calculations addressing the role of surface ligands, equivalent to the treatment of CdSe by Pokrant *et al.*⁴, would be extremely valuable.

Another way to probe the role of the surfaces is to intentionally trap or remove carriers from the core of the QD by application of quenching or scavenger groups. Utilized in conjunction with optical spectroscopies, this is a valuable way to link changes in electron and/or hole localization to modifications in the optical properties; as was done in ultrafast measurements examining the Auger-like relaxation mechanism in CdSe and InP QDs.⁵⁻⁷

The optical properties of CdSe NCs have been significantly improved by capping with a wider band gap material and is attributed to the increased confinement of the carriers in the core of the QD. The core/shell structures of the IV-VI semiconductors have only recently become available⁸ but it would be interesting to compare the emission properties and carrier dynamics of these structures to the bare PbSe QDs to see if enhanced electron and hole confinement impacts the results present in Chapters 4 and 5.

The optical properties of arrays of PbSe QD should also be a very interesting topic of research. The preliminary studies on close-packed PbSe NC assemblies have already yielded very encouraging results concerning interdot dipole-dipole interactions. Future studies could include the incorporation of QD solids into photonic crystal structures specifically designed to control light on the micrometer scale or studies of the optomagnetic properties of PbSe - Fe₂O₄ nanoparticle superlattices.⁹

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Chapter 7 Appendix

Interband transition quadrupole matrix element for lead-salt quantum dots

The transition dipole matrix elements have been calculated previously within the 4-band envelope function formalism.¹ This appendix is not intended as an introduction to envelope function electronic structure calculations. Rather, it is intended as an extension to this prior work. We have strived for consistency of notation and where deviations were necessary, a note will made.

The starting point is the interband transition matrix element to be evaluated.

$$\langle \psi_{C}(\mathbf{r}) | e^{i\mathbf{k}\cdot\mathbf{r}} \hat{\mathbf{p}} | \psi_{V}(\mathbf{r}) \rangle \cdot \mathbf{e} A(\mathbf{r},t)$$
 (7.1)

By expanding the exponential we recognize the first term as the electric dipole contribution,

$$\langle \psi_{C}(\mathbf{r})|\hat{\mathbf{p}}|\psi_{V}(\mathbf{r})\rangle \cdot \mathbf{e}A(\mathbf{r},t)$$
 (7.2)

while the second term contains both electric quadrupole and magnetic dipole contributions.

$$i\mathbf{k}\cdot\langle\psi_{C}(\mathbf{r})|\hat{\mathbf{rp}}|\psi_{V}(\mathbf{r})\rangle\cdot\mathbf{e}A(\mathbf{r},t)$$
 (7.3)

Let us concentrate on this second term. The operator is re-expressed as a sum of symmetric and anti-symmetric contributions,

$$\hat{\mathbf{r}}\hat{\mathbf{p}} = \frac{1}{2}\left(\hat{\mathbf{r}}\hat{\mathbf{p}} + \hat{\mathbf{p}}\hat{\mathbf{r}}\right) + \frac{1}{2}\left(\hat{\mathbf{r}}\hat{\mathbf{p}} - \hat{\mathbf{p}}\hat{\mathbf{r}}\right)$$
(7.4)

which are shown² to be the electric quadrupole response (symmetric term) and the magnetic dipole response (anti-symmetric term). Applying the identity,

$$\hat{\mathbf{r}}\hat{\mathbf{p}} + \hat{\mathbf{p}}\hat{\mathbf{r}} = \frac{im_e}{\hbar} \left[\hat{H}_0, \hat{\mathbf{r}}\hat{\mathbf{r}} \right]$$
(7.5)

to the electric quadrupole term yields,

$$\frac{-m_e}{2\hbar} (E_C - E_V) \mathbf{k} \cdot \langle \boldsymbol{\psi}_C(\mathbf{r}) | \hat{\mathbf{r} \mathbf{r}} | \boldsymbol{\psi}_V(\mathbf{r}) \rangle \cdot \mathbf{e} A(\mathbf{r}, t)$$
(7.6)

which results a more standard form of the quadrupole operator (dyadic product of position operators). The magnetic dipole contribution is ignored.³

For Pb-salt QDs, the wavefunction of conduction and valence electrons are expanded with the same set of band-edge Bloch functions,¹

$$\left| \psi_{C,V} \left(\mathbf{r} \right) \right\rangle = F_1 \left(\mathbf{r} \right) \left| z \uparrow \right\rangle + F_2 \left(\mathbf{r} \right) \left| z \downarrow \right\rangle + F_3 \left(\mathbf{r} \right) \left| -iR \uparrow \right\rangle + F_4 \left(\mathbf{r} \right) \left| +iR \downarrow \right\rangle$$

$$(7.7)$$

Evaluating the matrix element between initial and final states,

$$\langle \boldsymbol{\psi}_{C}(\mathbf{r})|\hat{\mathbf{rr}}|\boldsymbol{\psi}_{V}(\mathbf{r})\rangle$$
 (7.8)

yields,

$$\int d^3 r \left[\sum_{i=1}^4 F_i^C(\mathbf{r}) u_i(\mathbf{r}) \right]^* \mathbf{rr} \left[\sum_{j=1}^4 F_j^V(\mathbf{r}) u_i(\mathbf{r}) \right]$$
(7.9)

Recall that the Bloch function are periodic over adjacent unit cells whereas the envelope functions are slowly-varying on that same length scale. Because of these properties, the integral over the QD volume splits into a sum of unit cell (UC) contributions and where q indexes the number of unit cells in the QD.

$$\left\langle \boldsymbol{\psi}_{C}\left(\mathbf{r}\right)\left|\hat{\mathbf{r}}\hat{\mathbf{r}}\right|\boldsymbol{\psi}_{V}\left(\mathbf{r}\right)\right\rangle \approx \sum_{i=1}^{4}\sum_{j=1}^{4}\sum_{q}F_{i}^{C}\left(\mathbf{R}_{q}\right)^{*}F_{j}^{V}\left(\mathbf{R}_{q}\right)$$

$$\left\{\int_{UC}d^{3}r'u_{i}\left(\mathbf{r'}\right)^{*}\left[\mathbf{r'r'}+\mathbf{r'R}_{q}+\mathbf{R}_{q}\mathbf{r'}+\mathbf{R}_{q}\mathbf{R}_{q}\right]u_{j}\left(\mathbf{r'}\right)\right\}$$
(7.10)

The unit cell integrals simplify according to the following relations established by Kang *et al.*¹

$$\int_{UC} d^3 \mathbf{r'} u_i \left(\mathbf{r'}\right)^* \mathbf{r'} u_j \left(\mathbf{r'}\right) \propto \mathbf{P}^{CV}$$
(7.11)

$$\int_{UC} d^3 r' u_i \left(\mathbf{r'}\right)^* u_j \left(\mathbf{r'}\right) \propto \delta_{ij}$$
(7.12)

where in the first integral, \mathbf{P}^{cv} is the bulk semiconductor dipole matrix element and the second integral established the orthonormality of the basis states. For the quadupole, the resulting unit cell integrals are similar,

$$\int_{UC} d^3 \mathbf{r'} u_i \left(\mathbf{r'}\right)^* \mathbf{r'r'} u_j \left(\mathbf{r'}\right) \equiv \mathbf{\vec{Q}}_{i,j}^{CV}$$
(7.13)

$$\int_{UC} d^3 \mathbf{r'} u_i \left(\mathbf{r'}\right)^* \mathbf{r'} \mathbf{R}_q u_j \left(\mathbf{r'}\right) \propto \mathbf{P}_{i,j}^{CV} \mathbf{R}_q$$
(7.14)

$$\int_{UC} d^3 \mathbf{r'} u_i \left(\mathbf{r'}\right)^* \mathbf{R}_q \, \mathbf{r'} u_j \left(\mathbf{r'}\right) \propto \mathbf{R}_q \mathbf{P}_{i,j}^{CV} \tag{7.15}$$

$$\int_{UC} d^3 r' u_i \left(\mathbf{r'}\right)^* \mathbf{R}_q \, \mathbf{R}_q u_j \left(\mathbf{r'}\right) \propto \mathbf{R}_q \mathbf{R}_q \delta_{ij} \tag{7.16}$$

Q^{cv} is a new quantity, defined in analogy to **P**^{cv}, it is the bulk crystal's quadrupole matrix element. Note that unlike **P**^{cv}, this parameter has no part in **k.p** calculations. To determine it would require direct evaluation of the unit cell integral using explicit forms of the basis states.

Making these notational substitutions in the quadrupole matrix element yields the following,

$$\left\langle \boldsymbol{\psi}_{C}\left(\mathbf{r}\right)\left|\hat{\mathbf{r}}\hat{\mathbf{r}}\right|\boldsymbol{\psi}_{V}\left(\mathbf{r}\right)\right\rangle \approx \sum_{i=1}^{4}\sum_{j=1}^{4}\int_{QD}d^{3}RF_{i}^{C}\left(\mathbf{R}\right)^{*}F_{j}^{V}\left(\mathbf{R}\right)*\left[\vec{\mathbf{Q}}_{i,j}^{CV}+\mathbf{P}_{i,j}^{CV}\mathbf{R}+\mathbf{R}\mathbf{P}_{i,j}^{CV}+\mathbf{R}\mathbf{R}\boldsymbol{\delta}_{ij}\right]$$

$$\left[\vec{\mathbf{Q}}_{i,j}^{CV}+\mathbf{P}_{i,j}^{CV}\mathbf{R}+\mathbf{R}\mathbf{P}_{i,j}^{CV}+\mathbf{R}\mathbf{R}\boldsymbol{\delta}_{ij}\right]$$
(7.17)

It is valuable to compare this result (7.17) to the corresponding electric dipole matrix element,

$$\left\langle \boldsymbol{\psi}_{C}\left(\mathbf{r}\right) \left| \hat{\mathbf{r}} \right| \boldsymbol{\psi}_{V}\left(\mathbf{r}\right) \right\rangle \approx \sum_{i=1}^{4} \sum_{j=1}^{4} \int_{QD} d^{3}R F_{i}^{C}\left(\mathbf{R}\right)^{*} F_{j}^{V}\left(\mathbf{R}\right) * \left[\mathbf{P}_{i,j}^{CV} + \mathbf{R}\delta_{ij}\right]$$
(7.18)

Notice that the dipole matrix element contains contributions from (1) the dipole moment of the Bloch functions and (2) the dipole moment of the envelope functions. Similarly by extension, the quadrupole matrix element contains contributions from (1) the quadrupole moment of the Bloch functions, (2) a combination of dipole moments of the Bloch functions and envelope function, and (3) the quadrupole moment of the envelope functions.

We estimated the magnitude of the electric dipole and electric quadrupole matrix elements. The electric dipole was numerically evaluated on a $S_e - S_h$ transition and the electric quadrupole, on a S – P transition. Without access to a numerical value for Q^{cv} , we approximated this with the square of P^{cv} . We find that the electric quadrupole and electric dipole are of the same order magnitude (~ 0.1). Therefore, the quadrupole contribution is a factor of ~ $1/\lambda$ smaller than the dipole. There is no way to explain a strong quadrupole feature in the linear absorption spectrum on the basis of the overlap integrals alone. The application of strong electric field gradients, discussed in Chapter 3, appears to be the only way to selectively enhance a quadrupole transition to a strength comparable to the electric dipole.

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