

ELECTRONIC STATES OF LEAD SALT NANOCRYSTAL AND NANOCRYSTAL ASSEMBLIES

A Dissertation

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ELECTRONIC STATES OF LEAD SALT NANOCRYSTAL AND NANOCRYSTAL ASSEMBLIES

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With the development of new synthetic methods, semiconductor nanocrystals of various morphologies and dimensions have been created. This changes their electro-optical properties, and brings new questions in understanding. At the same time, more and more research is now focused on nanocrystal assemblies, in particular nanocrystal superlattices with atomically coherent lattices, with the potential for various optoelectronic device applications.

This thesis examines, in both theory and experiment, a number of nanocrystal systems, with the stress on dimensionality and morphology. In particular, in 1D and 2D systems, due to the anisotropic quantum confinement, the electrons and holes will form a tightly bound excitons, even at room temperature, in contrast to 0D and 3D systems, where either quantum confinement or coulomb interaction completely dominates. We'll also look into nanocrystal assemblies, both amorphous and atomically coherent, and study the effect of the inherent disorder in the structure on their electronic properties, with the goal of charge transportation through delocalized states. Last, we'll examine the fine structure in these nanocrystals.

BIOGRAPHICAL SKETCH

Jun Yang was born in Shanghai, China in 1987. From his early ages, he developed great interest in mathematics, which later turned into more concrete forms of computer science and physics. During high school, he attended national competitions, which allowed him to attend Peking University without taking the national entrance exam.

During the four years of study of physics in Peking University, he developed a solid foundation of general physics knowledge, but found that the college education alone is not enough to satisfy his curiosity in the subject, and yearned to learn more. He therefore came to the United States in 2009 and continued his study in Cornell University.

Jun Yang joined the Frank Wise group in 2010, and studied semiconductor nanocrystals from then on. He enjoyed enormously the years spent there. After graduation, he will be a postdoctoral researcher in Corning Inc.

To my parents, for their great sacrifice and unconditional love.

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CHAPTER 1

INTRODUCTION

Semiconductor nanocrystals (NCs, also known as quantum dots, QDs) are particles that are usually a few nanometers in size, and consist of hundreds to thousands of atoms. They are too big to be analyzed as large molecules, yet too small to behave exactly like the bulk semiconductors. Their intermediate sizes give them unique electrical and optical properties, and have raised significant research interest in the last 20 years.

One way to understand their energy levels is to start from the molecular orbitals, and bring them together. The bonding and antibonding orbitals push each other away, giving rise to this discrete set of energy levels (see Figure 1.1). The atomistic tight-binding model is an approximate but feasible implementation of this approach.[1] We'll come back to this model later.

The opposite way to understand is to start from the bulk semiconductor, and use a simple quantum mechanics model of a particle in the box: when an electron is confined in a finite region, the energy levels that it can occupy becomes discrete. The smaller the box is, the larger the average separation of these energy levels become.(see Figure 1.1) This phenomenon is called quantum confinement, thus giving the name of quantum dots.[2] The envelope function theory is the systematic way of calculating these energy levels,[3] and we'll discuss them in more details later.

At what size is quantum confinement significant enough that it should be included? There are two major criteria. First, when the separation of the energy levels $\hbar^2\pi^2/(2mL^2)$ becomes larger than the thermal energy k_BT , the discrete en-

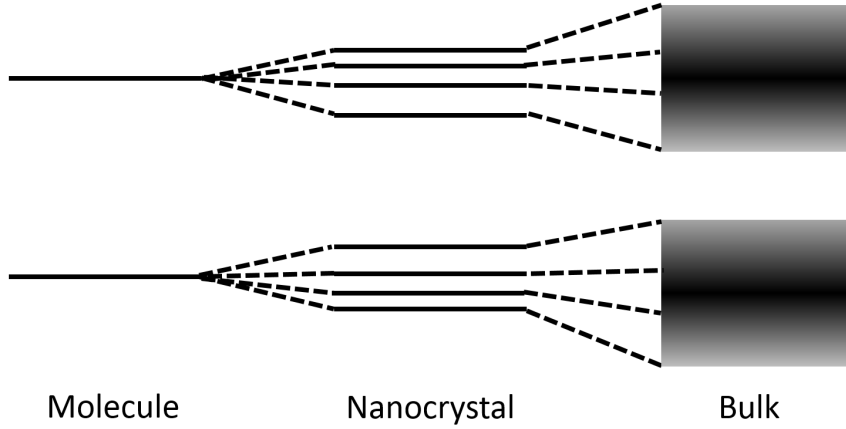


Figure 1.1: Nanocrystal as an intermediate regime of molecule and bulk semiconductor.

ergy levels start to affect the thermally induced charge distribution.[4] For typical semiconductors, the characteristic size $\pi\hbar/\sqrt{m^*k_B T}$ is on the order of 10 nm. Thus nanocrystals of this size or below should be considered as strongly quantum confined. Another criterion is to compare the nanocrystal size with the Bohr radius of the exciton. Suppose the binding energy of the exciton in the bulk semiconductor is larger than thermal energy, and the excited electron and hole form a bound exciton. If the size of the nanocrystal is smaller than the exciton Bohr radius $a_{Bohr}\epsilon_r/m^*$, the quantum confinement effect dominates the exciton coulomb binding, and the nanocrystal is in the strongly confined regime. Typical semiconductors has Bohr radius of a few to tens of nanometers.

The first semiconductor NCs were made in the early 1980s in glass matrices,[5, 6, 7] by dissolving a small fraction of the semiconductor phase in the silicate glass. After secondary heat treatment, nucleation and growth of semiconductor NCs occurred as a result of diffusive phase decomposition of supersaturated solid solution. Almost at the same time but independently, Brus and his coworkers in Bell Labs discovered colloidal synthesis of cadmium sulfide (CdS) NCs,[8, 9] by slowly mix-

ing a dilute Cd^{2+} solution and S^{2-} solution at higher concentration in water, or acetonitrile. NCs in these early stages suffered from large size distribution, and poor surface passivation, and therefore only a limited amount of optical and electrical studies ensued. It was not until 1993, when Murray in MIT discovered a hot injection method,[10] and achieved $< 5\%$ rms in diameter after size selective precipitation, that QDs really started to attract attention and extensive research. Efficient, high quality colloidal synthesis makes it possible to achieve potentially large volume, low cost, and highly versatile production of NCs in various media. Currently, NCs of all kinds of shapes (0D, 1D, 2D, forked, faceted), composition (II-VI, IV-VI, III-V, core-shell, alloyed, gradient) as well as highly complicated heterostructures have been made, most of which are based on the hot injection method.

Lead salt NCs, particularly lead sulfide (PbS) and lead selenide (PbSe), deserves special attention. In the early development of NCs, they did not attract similar attention as II-VI semiconductors. The hot injection method for lead salt was not discovered until 2001.[11] On the other hand, their bulk band structure is significantly different from II-VI and III-V semiconductors. First, they have a direct bandgap at the four L-points in the Brillouin zone. Plus the two-fold spin degeneracy, their conduction and valence band-edge are both eight-fold degenerate. This large degeneracy makes it possible to have multiple carriers in the lowest energy states, opening the possibility of efficient multiple exciton generation and extraction. Second, unlike II-VI and III-V semiconductors, the conduction and valence band at the band extrema for lead salts are nearly symmetric, and well separated from the next band. This means that both the electron and hole will be in the strong confinement regime, with well separated energy levels. Third, lead salt semiconductors are highly polarizable. The optical dielectric constants for

PbS and PbSe are 17 and 23, and their static dielectric constants are even larger. Coulomb interaction in these materials is highly screened, which results in very large Bohr radius, and strongly confined electrons and holes in the NCs. Last, the near infrared bandgap of lead salt NCs is ideal for solar energy harvesting, optical communication applications.

Their tunable energy gaps, easy access to surface modification, and relatively cheap cost of manufacturing makes NCs attractive for a number of optoelectronic devices, such as solar cells,[12, 13, 14, 15] light-emitting diodes,[16, 17] photodetectors,[18, 19] and photocatalysts,[20] to name a few. All these applications require efficient light emission or absorption, as well as efficient charge extraction and charge transport. In order to achieve this, great amount of work has been done on the surface chemistry to optimize the surface qualities of these NCs while bringing NCs closer to each other to optimize transport.

At the same time, new colloidal synthetic methods are developed to create NCs of different dimensions: 1D, 2D or quasi-3D structures. These structures can potentially have much better transport properties than 0D structures, while maintaining the quantum confinement and solution processability. The focus of this thesis is to study the electronic state of these novel 0D, 1D, 2D or quasi-3D nanostructures, both in theory and experiments.

1.1 Organization of the Dissertation

The rest of the thesis is organized as follows. Starting from section 1.2, we'll briefly introduce the envelope function and the $\mathbf{k} \cdot \mathbf{p}$ perturbation theory, which are the basics of studying the energy levels of isolated nanocrystals. In chapter 2, we'll illustrate the method by calculating the energy levels for lead salt nanocubes

and nanosheets. The synthesis of small nanocubes was recently developed in our lab, and nanocubes are the ideal building blocks of 3D nanocrystal solids. The synthesis of lead salt nanosheets was also developed recently, and as a 2D material, it has significantly different electronic structure. In the lateral direction, where the quantum confinement no longer exists, the coulomb interaction dominates, and 2D excitons are formed. Due to the reduced dielectric screening, the coulomb interaction is furthermore strengthened compared with bulk semiconductors.

In chapter 3, we'll look at nanocrystal assemblies, in particular how the inherent disorder in these metamaterials affects their transport properties. We'll use a simplified tight binding model, which explicitly models the size dispersity and packing disorder in the assembly, and calculate the wavefunction extension. We'll introduce the quantity fractal dimension, which is used to evaluate whether a particular electronic state is localized or delocalized. We'll illustrate the result by comparing it with the qualities of the NC solids that are currently available. We'll also discuss the effect of the eight-fold degeneracy in lead salt NCs on the delocalization. Furthermore, we'll discuss delocalization in a quasi-2D nanostructure, the newly developed atomically coherent NC superlattices. We'll end this chapter by discussing the relationship of localization length and fractal dimension.

In chapter 4, we'll look into the electronic state in 1D nanorod. Previous theoretical study has predicted exciton formation at room temperature for these nanocrystals. We'll use optical spectroscopy to study the exciton relaxation dynamics in these nanorods, and compare it with 0D nanocrystals. We find that the results do agree with the picture of tightly bound exciton.

In chapter 5, we'll use various optical spectroscopy to study the fine structure of lead salt nanocrystals. More specifically, we will focus on the origin of the tem-

perature dependent Stokes shift of the photoluminescence of these nanocrystals. As a side product, we discover a transient exciton state even when the nanocrystals are excited at the energy gap, and associate it with the polaron formation.

In the last chapter, we'll discuss some future directions.

1.2 Envelope Function Theory

The envelope function approximation was first studied by Wannier[21] and Slater,[3] and later by Luttinger and Kohn.[22] Slater's method expands the total wave functions in Wannier functions. Luttinger and Kohn's method expands the wave functions in Bloch functions at the band extrema. We'll describe Luttinger and Kohn's theory here. Suppose the unperturbed Hamiltonian for an infinite periodic lattice is $H_0(\mathbf{r})$. According to Bloch's theorem, for an infinite perfect crystal, the eigen wave functions can be written as $\psi_{n\mathbf{k}}(\mathbf{r})$ which satisfies

$$H_0(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}) = E_n(\mathbf{k}) \psi_{n\mathbf{k}}(\mathbf{r}) \quad (1.1)$$

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (1.2)$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is a periodic function with the same periodicity as the crystal. The goal is to find functions $\psi(\mathbf{r})$ that satisfies

$$H(\mathbf{r}) \psi(\mathbf{r}) = [H_0(\mathbf{r}) + H_1(\mathbf{r})] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (1.3)$$

where $H_1(\mathbf{r})$ is a slowly varying function of $\mathbf{r}$ (i.e., the fractional change of $H_1(\mathbf{r})$ over a unit cell is small) Luttinger and Kohn [22] proved that if we expand the wave function in terms of band extrema (at $\mathbf{k}_0$) Bloch functions,

$$\psi(\mathbf{r}) = \sum_n F_n(\mathbf{r}) \psi_{n\mathbf{k}_0}(\mathbf{r}) \quad (1.4)$$

then $F_n(\mathbf{r})$ satisfies the following differential equation

$$[E_n(\mathbf{k}_0 - i\nabla) + H_1(\mathbf{r})] F_n(\mathbf{r}) = E F_n(\mathbf{r}) \quad (1.5)$$

Here the first term $E_n(\mathbf{k}_0 - i\nabla)$ stands as an abbreviation for the differential operator in which $E_n(\mathbf{k}_0 + \mathbf{k})$ is transformed by replacing $\mathbf{k}$ with $-i\nabla$.

The envelope function theory relies on the assumption of a slowly varying perturbation. On the other hand, it is frequently used to analyze materials with atomically abrupt interfaces. The initial solution was to solve the envelope function away from the interface individually, and use some *ad hoc* boundary conditions to stitch them together.[23] Later, Burt published a series of papers deriving the boundary conditions in a more systematic way.[24, 25]

To sum up, given the dispersion curve $E_n(\mathbf{k})$ of the semiconductor bandstructure, we effectively reduce the problem of electrons in a periodic lattice and additional perturbing potential to a simpler problem of free electrons with a particular dispersion relation in the perturbing potential.

1.3 $\mathbf{k} \cdot \mathbf{p}$ Perturbation Theory in Crystalline Solids

In order to use Eq 1.5 to calculate the electronic states, we need an analytic expression for $E_n(\mathbf{k})$ for the bulk material. This is generally very hard as the bandstructure of semiconductors can be very complicated in the Brillouin zone, with many dips and peaks. On the other hand, the bottom of the conduction band or the top of the valence band usually has just one or a few degenerate extrema. If the electron or hole has small energy, their wave functions mostly concentrate around these extrema. Thus if we can model the bandstructure accurately around

the extrema, we'll get a good approximation of the bandstructure. And here comes the $\mathbf{k} \cdot \mathbf{p}$ theory.[26, 27, 28]

Back to the Schrödinger Equation

$$H_0(\mathbf{r}) \psi_n(\mathbf{k}, \mathbf{r}) = E_n(\mathbf{k}) \psi_n(\mathbf{k}, \mathbf{r}) \quad (1.6)$$

with the Hamiltonian which includes the spin-orbit coupling

$$H_0(\mathbf{r}) = \frac{\mathbf{p}^2}{2m_0} + V(\mathbf{r}) + \frac{\hbar^2}{4m_0^2 c^2} (\boldsymbol{\sigma} \times \nabla V) \cdot \mathbf{p} \quad (1.7)$$

and the Bloch wave function

$$\psi_n(\mathbf{k}, \mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_n(\mathbf{k}, \mathbf{r}) \quad (1.8)$$

For simplicity, let's assume that the band extremum is at $\mathbf{k} = \mathbf{0}$. Suppose we already know $E_n(\mathbf{0})$ and $u_n(\mathbf{0}, \mathbf{r})$ for all bands close to the bandgap, we would like to calculate $E_n(\mathbf{k})$ for an arbitrary $\mathbf{k}$ in the proximity of $\mathbf{0}$. Plugging Eq 1.8 into Eq 1.6, and using Eq 1.7, we obtain the equation for $u_n(\mathbf{k}, \mathbf{r})$:

$$\begin{aligned} \left(\frac{\hbar^2 \mathbf{k}^2}{2m_0} + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} + \frac{\mathbf{p}^2}{2m_0} + V(\mathbf{r}) + \frac{\hbar}{4m_0^2 c^2} (\boldsymbol{\sigma} \times \nabla V) \cdot (\hbar \mathbf{k} + \mathbf{p}) \right) u_n(\mathbf{k}, \mathbf{r}) \\ = E_n(\mathbf{k}) u_n(\mathbf{k}, \mathbf{r}) \end{aligned} \quad (1.9)$$

With the notation

$$\boldsymbol{\pi} \equiv \mathbf{p} + \frac{\hbar}{4m_0 c^2} (\boldsymbol{\sigma} \times \nabla V) \quad (1.10)$$

Eq 1.9 becomes

$$\underbrace{[H_0(\mathbf{r}) + \frac{\hbar^2 \mathbf{k}^2}{2m_0} + \frac{\hbar}{m_0} \mathbf{k} \cdot \boldsymbol{\pi}]}_W u_n(\mathbf{k}, \mathbf{r}) = E_n(\mathbf{k}) u_n(\mathbf{k}, \mathbf{r}) \quad (1.11)$$

where we obtain two extra terms. One is a constant shift of the energy; the other is proportional to $\mathbf{k} \cdot \mathbf{p}$ (in the case of no spin orbit coupling), thus giving rise to the name $\mathbf{k} \cdot \mathbf{p}$ theory. Here we derive a “Schrödinger Equation” for $u_n(\mathbf{k}, \mathbf{r})$ instead

of $\psi_n(\mathbf{k}, \mathbf{r})$ is because $u_n(\mathbf{k}, \mathbf{r})$ is periodic with respect to the crystal lattice while $\psi_n(\mathbf{k}, \mathbf{r})$ is not.

If we consider nondegenerate bands and weak coupling between adjacent bands, we can use 2^{nd} order perturbation theory and get

$$E_n(\mathbf{k}) \approx E_n(\mathbf{0}) + \frac{\hbar^2 \mathbf{k}^2}{2m_0} + \frac{\hbar^2}{m_0^2} \sum_{n' \neq n} \frac{|\langle u_n(\mathbf{0}, \mathbf{r}) | \mathbf{k} \cdot \boldsymbol{\pi} | u_{n'}(\mathbf{0}, \mathbf{r}) \rangle|^2}{E_n(\mathbf{0}) - E_{n'}(\mathbf{0})} \quad (1.12)$$

Since $\mathbf{k}$ here is just a parameter, we can take it outside. The rest of the matrix element $\langle u_n(\mathbf{0}, \mathbf{r}) | \boldsymbol{\pi} | u_{n'}(\mathbf{0}, \mathbf{r}) \rangle$ is the Kane momentum-matrix element between the unperturbed wave functions, and can be easily parameterized.

If we consider strong coupling between bands, then instead of using the perturbation theory as in Eq 1.12, we need to diagonalize the matrix with each component corresponding to coupling between different bands, and we get the multi-band $\mathbf{k} \cdot \mathbf{p}$ model.

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CHAPTER 2

ELECTRONIC STATES OF NANOCRYSTALS

2.1 Introduction

The electronic states are first and foremost the most important aspect of a semiconductor nanocrystal. The central idea of quantum confinement relies on our ability to change the energy of the electronic states by changing the size and shape of the nanocrystals. In a NC light emitting diode, the wavelength they emit depends on their bandgap energy; in a photovoltaic or photocatalysis device, the absorption efficiency and energy transfer efficiency depends critically on the position of the energy levels.[1] In addition, it's not only their energy, but also the shape of the wave function that is important. The selection rules of linear and nonlinear optical transitions depend on the symmetry of the wave functions.[2, 3] The coupling between nanocrystal and its environment, albeit it being the surface defects,[4] or charge conducting material,[5] or another nanocrystal,[6, 7] depends on the wave function extension at the interface. The carrier relaxation also depends on the exact form of the ground state and excited state wave functions.[8, 9]

The energy levels for lead-salt NCs have been calculated using many methods, including envelope function theory,[2] atomistic tight binding,[10, 11] atomistic pseudopotential,[12] and *ab-initio* density functional theory (DFT).[13, 14] Among all these, only the density functional theory considers the equilibrium position of the atoms as well as the electronic states, thus ideally gives the most complete description. It is also the only *ab-initio* method, thus requiring no prior knowledge of the band structure. On the other hand, any feasible implementation requires approximating the exchange and correlation interactions, which brings uncertain-

ties to the result. Also, the original DFT theory could only calculate ground state energy, although time-dependent DFT was developed later to describe excited states. The atomistic tight binding and atomistic pseudopotential method both fit the bulk band structure of the semiconductor to a truncated effective model, and then use this effective model to calculate the electronic state of a finite-size NC. The quality of their results depends on how close the fitted model is to the actual band structure. This usually depends on the number of basis used, thus one needs to balance the tradeoff between accuracy and efficiency. Both methods treat each atom individually, and thus are computationally intensive and generally apply only to individual small NC.

Compared with these methods, envelope function theory is the most intuitive and most efficient to implement. It is based on the idea that the electron wave function of a NC can be decomposed into a product of a fast-varying part (periodic with respect to the crystal lattice) and a slow-varying envelope function. The envelope function satisfies an effective Hamiltonian, as well as appropriate boundary conditions which depend on the size and shape of the NC. It turns out that with the proper envelope Hamiltonian and appropriate boundary conditions, envelope function theory produces quite accurate results in calculating the ground and excited states of NCs of different compositions,[15, 2, 16] sizes and shapes.[17, 18] It also provides the correct symmetry of the wave functions. Combined with the intuitive physical picture it provides, envelope function theory is frequently used in analyzing more complex carrier dynamics, such as electron-phonon coupling,[19] Auger recombination,[9] multiple exciton generation,[20] *etc.*

In this chapter, we'll use the four band $\mathbf{k} \cdot \mathbf{p}$ model to calculate energy levels of lead salt nanocubes and nanosheets, both of which have their own research interest.

Results presented in the section on nanocubes have been published in Ref [21].

2.2 Four-band $\mathbf{k} \cdot \mathbf{p}$ Model for Lead Salts

The most accurate model used to describe the band structure near band extremum L points for lead salts is the $\mathbf{k} \cdot \mathbf{p}$ model developed by Mitchell and Wallis[22] and Dimmock[23]. This model has been used successfully to explain the energy levels for lead salt quantum dots,[2] quantum rods,[17] and core-shell structures.[16] The 4-band Hamiltonian in the isotropic approximation is

$$H_0(\mathbf{k}) = \begin{pmatrix} \left(\frac{E_g}{2} + \frac{\hbar^2 \mathbf{k}^2}{2m^-}\right) \mathbf{I} & \frac{\hbar P}{m} \mathbf{k} \cdot \boldsymbol{\sigma} \\ \frac{\hbar P}{m} \mathbf{k} \cdot \boldsymbol{\sigma} & -\left(\frac{E_g}{2} + \frac{\hbar^2 \mathbf{k}^2}{2m^+}\right) \mathbf{I} \end{pmatrix} \quad (2.1)$$

which is a 4×4 matrix, where P is the Kane momentum-matrix element between the extremal valence- and conduction-band states; m^- and m^+ are the far-band contributions to the band-edge effective masses; m is the free electron mass; $\boldsymbol{\sigma}$ is the Pauli matrix. All parameters in the calculation uses the values in ref [2], which are listed in Table 2.1.

Material	$E_g(T = 300K)$ (eV)	m/m^-	m/m^+	$2P^2/m$ (eV)
PbS	0.41	2.5	3.0	2.5
PbSe	0.28	3.9	6.9	2.6

Table 2.1: Band paramters used in 4-band $\mathbf{k} \cdot \mathbf{p}$ effective mass model for PbS and PbSe.

The quantum confined energy levels are obtained by solving the envelope function equation with imposed boundary condition

$$H_0(-i\nabla) \mathcal{F}(r) = E \mathcal{F}(r) \quad (2.2)$$

where the envelope wave function $\mathcal{F}(r)$ is a four component vector $[F_j(r)]$, $j = 1 \dots 4$.

2.3 Lead Salt Nanocubes

Sub-10 nm monodisperse PbS nanocubes were first synthesized in our labs.[21] Previous methods have successfully synthesized lead salt nanocubes but only of relatively large sizes (> 10 nm).[24, 25, 26, 27] One important application for nanocubes is that they form superlattices with higher packing ratio, as well as stronger inter-particle coupling compared with their spherical counterparts.[6] In order to achieve strong coupling, the nanocrystals themselves have to be in strong confinement, and the smaller the size the stronger the coupling will be. Thus, making small and monodisperse nanocubes is critical in their applications.

The method we used was post-synthesis shape engineering, by reacting at room temperature existing quasi-spherical PbS NCs with anhydrous $(\text{NH}_4)_2\text{S}$ in a solution of primary amine. The original NCs are passivated by oleic acid (OA), a long hydrocarbon chain. In the reaction $(\text{NH}_4)_2\text{S}$ converts surface lead oleate ($\text{Pb}(\text{OA})_2$) into PbS, which is then redistributed on the surface via facet growth. Due to the high reactivity of (111) facets compared with (100) facets, the majority of newly formed PbS are deposited at the corner, thus forming the cubic shape.

In order to collaborate with structural characterization, that the nanocube is indeed single crystalline, and the electron is delocalized in the entire nanocube, we need to calculate the energy levels of the quantum confined states and compare them with experiments.

2.3.1 Ansatz Solution

The boundary condition for isolated NCs is to assume that the wave function approaches 0 at the boundary, due to the insulating nature of the passivating organic ligands on the surface. The same boundary condition was used in calculating other NCs.[2, 16, 17] For nanocubes, these show up as

$$\mathcal{F}(\mathbf{r}_i = 0, L) = 0, \quad \text{for } i = x, y, z \quad (2.3)$$

It is not clear whether a closed-form solution exists at all. However, it can always be expanded in a set of basic functions that satisfy the boundary conditions

$$F_j(r) = \sum_{\alpha, \beta, \gamma > 0} A_{j, \alpha, \beta, \gamma} \sin\left(\frac{\alpha\pi x}{L}\right) \sin\left(\frac{\beta\pi y}{L}\right) \sin\left(\frac{\gamma\pi z}{L}\right) \quad (2.4)$$

where α, β, γ are all natural numbers. Plugging Eq.2.4 into the Schrödinger's Equation 2.2, and using the orthogonal relations:

$$\int_0^\pi \sin \alpha x \sin \beta x dx = \frac{\pi}{2} \delta_{\alpha\beta} \quad (2.5a)$$

$$\int_0^\pi \sin \alpha x \cos \beta x dx = \begin{cases} 0 & , \text{ if } \alpha + \beta \text{ is even} \\ \frac{2\alpha}{\alpha^2 - \beta^2} & , \text{ otherwise} \end{cases} \quad (2.5b)$$

we obtain a set of coupled equations for the coefficients $A_{j,\alpha,\beta,\gamma}$:

$$\begin{aligned} \frac{4\hbar P}{mL} & \left[-i \sum_{\gamma}' A_{3,\alpha_0,\beta_0,\gamma} \frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2} - i \sum_{\alpha}' A_{4,\alpha,\beta_0,\gamma_0} \frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} - \sum_{\beta}' A_{4,\alpha_0,\beta,\gamma_0} \frac{\beta\beta_0}{\beta_0^2 - \beta^2} \right] \\ & = \left[E - \frac{E_g}{2} - \frac{\hbar^2 \pi^2}{2m^- L^2} (\alpha_0^2 + \beta_0^2 + \gamma_0^2) \right] A_{1,\alpha_0,\beta_0,\gamma_0} \end{aligned} \quad (2.6a)$$

$$\begin{aligned} \frac{4\hbar P}{mL} & \left[-i \sum_{\alpha}' A_{3,\alpha,\beta_0,\gamma_0} \frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} + \sum_{\beta}' A_{3,\alpha_0,\beta,\gamma_0} \frac{\beta\beta_0}{\beta_0^2 - \beta^2} + i \sum_{\gamma}' A_{4,\alpha_0,\beta_0,\gamma} \frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2} \right] \\ & = \left[E - \frac{E_g}{2} - \frac{\hbar^2 \pi^2}{2m^- L^2} (\alpha_0^2 + \beta_0^2 + \gamma_0^2) \right] A_{2,\alpha_0,\beta_0,\gamma_0} \end{aligned} \quad (2.6b)$$

$$\begin{aligned} \frac{4\hbar P}{mL} & \left[-i \sum_{\gamma}' A_{1,\alpha_0,\beta_0,\gamma} \frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2} - i \sum_{\alpha}' A_{2,\alpha,\beta_0,\gamma_0} \frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} - \sum_{\beta}' A_{2,\alpha_0,\beta,\gamma_0} \frac{\beta\beta_0}{\beta_0^2 - \beta^2} \right] \\ & = \left[E + \frac{E_g}{2} + \frac{\hbar^2 \pi^2}{2m^+ L^2} (\alpha_0^2 + \beta_0^2 + \gamma_0^2) \right] A_{3,\alpha_0,\beta_0,\gamma_0} \end{aligned} \quad (2.6c)$$

$$\begin{aligned} \frac{4\hbar P}{mL} & \left[-i \sum_{\alpha}' A_{1,\alpha,\beta_0,\gamma_0} \frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2} + \sum_{\beta}' A_{1,\alpha_0,\beta,\gamma_0} \frac{\beta\beta_0}{\beta_0^2 - \beta^2} + i \sum_{\gamma}' A_{2,\alpha_0,\beta_0,\gamma} \frac{\gamma\gamma_0}{\gamma_0^2 - \gamma^2} \right] \\ & = \left[E + \frac{E_g}{2} + \frac{\hbar^2 \pi^2}{2m^+ L^2} (\alpha_0^2 + \beta_0^2 + \gamma_0^2) \right] A_{4,\alpha_0,\beta_0,\gamma_0} \end{aligned} \quad (2.6d)$$

Here, the summation $\sum_{\alpha}' A_{i,\alpha,\beta_0,\gamma_0} \frac{\alpha\alpha_0}{\alpha_0^2 - \alpha^2}$ sums over all the natural numbers α that have a different parity with α_0 in the denominator. These coupled equations constitute an eigenvalue problem through which we can obtain the energies and wave functions for different states.

It is expected that for low energy states, there will be very small contributions from bases that have large momentum (high energy). Therefore, in order to calculate energy of states close to the band edge, one only needs to account for a limited number of basic functions to give a satisfactory solution. In any case, when the energy is too large, the $\mathbf{k} \cdot \mathbf{p}$ model itself is in question. Here we use a simple cutoff number N , and count only basic function with $1 \leq \alpha, \beta, \gamma \leq N$. This corresponds to the total of $4 \times N^3$ basic functions.

Figure 2.1 shows the convergence on the cutoff N , the number of basic functions used in the calculation for 4.2 nm length cube. One can see that the result converges quickly. One interesting thing is that the error depends critically on the parity

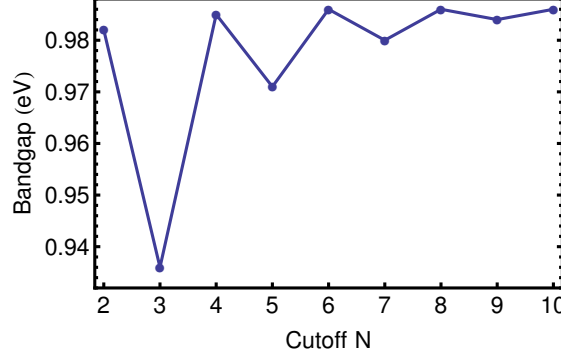


Figure 2.1: Convergence of bandgap energy calculated for PbS cube 4.2 nm in length, with different cutoff order for the basic functions.

of the number of basis. Calculations with odd number of bases systematically underestimate the bandgap, and have larger error than the ones with even number of bases. For the rest of the calculation, $N = 8$ is used.

Figure 2.2a shows the energy of states calculated for 4.2 nm length PbS cubes for the first 30 states. It is clear that the degeneracy of states is very similar to what one would expect from an even simpler 1-band model. The first two states in the conduction band are labeled $(n_x n_y n_z)_e = (111)_e$ states with spin degeneracy; the next six states are $(112)_e$; next group corresponds to $(122)_e$. To look more closely, the $(112)_e$ group has a small splitting of degeneracy, into four states with slightly smaller energy, and two states with higher energy. This is very similar to PbS spheres,[2] where $j = 3/2$, $\pi = 1$ has four fold degeneracy and $j = 1/2$, $\pi = 1$ state has two fold degeneracy, but has slightly higher energy. Both states can be assigned to p orbital (orbital angular momentum $l = 1$) but with different total angular momentum ($j = 1/2$ or $j = 3/2$). The splitting is due to spin-orbit interaction. This should be the case for PbS cubes as well. The cross sections of the envelope wave functions for the electron are plotted in Figure 2.3. The hole states are more or less mirror image of electron states due to the nearly symmetric conduction band and valence band in lead sulfide band structure. Figure 2.2b

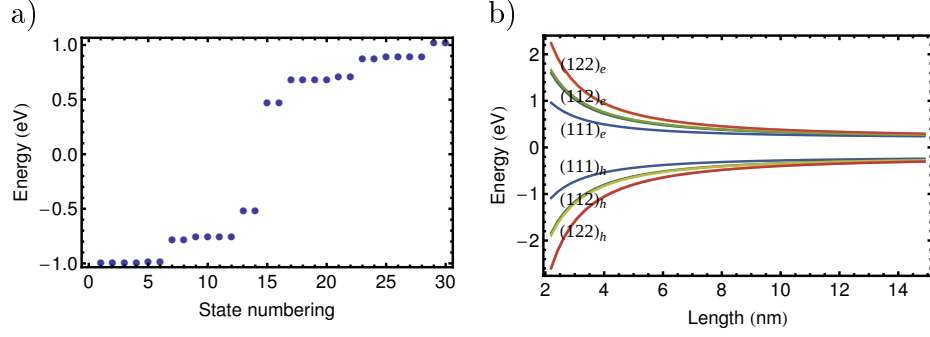


Figure 2.2: (a) Energies of the first 30 states for PbS cube 4.2 nm in length (b) Energies for the first 14 states for electron and hole as a function of length for PbS cube.

summarizes energy for the 10 lowest unoccupied states and 10 highest occupied states as a function of length of the cubes.

We try to find a simple analytic expression that can describe the bandgap reasonably well, to facilitate future comparison. In Figure 2.4a, calculated bandgaps (blue dots) are fitted to the function

$$E_{PbS}(a) = 0.41 + \frac{1}{0.149a + 0.061a^2} \quad (2.7)$$

where a is the length of the cube. We calculate, in the same way, bandgap for PbSe cubes (Figure 2.4b) for future reference, and fitted it to

$$E_{PbSe}(a) = 0.28 + \frac{1}{0.060a + 0.049a^2} \quad (2.8)$$

2.3.2 Comparison with Experiments

Figure 2.5 shows the structural and optical characterization of the nanocubes of three different sizes. Compared with the original spherical particles (Figure 2.5(a,b,c) insets, in the same magnification), the nanocubes definitely show more pronounced edges and cubic shape. The length of the nanocubes are slightly

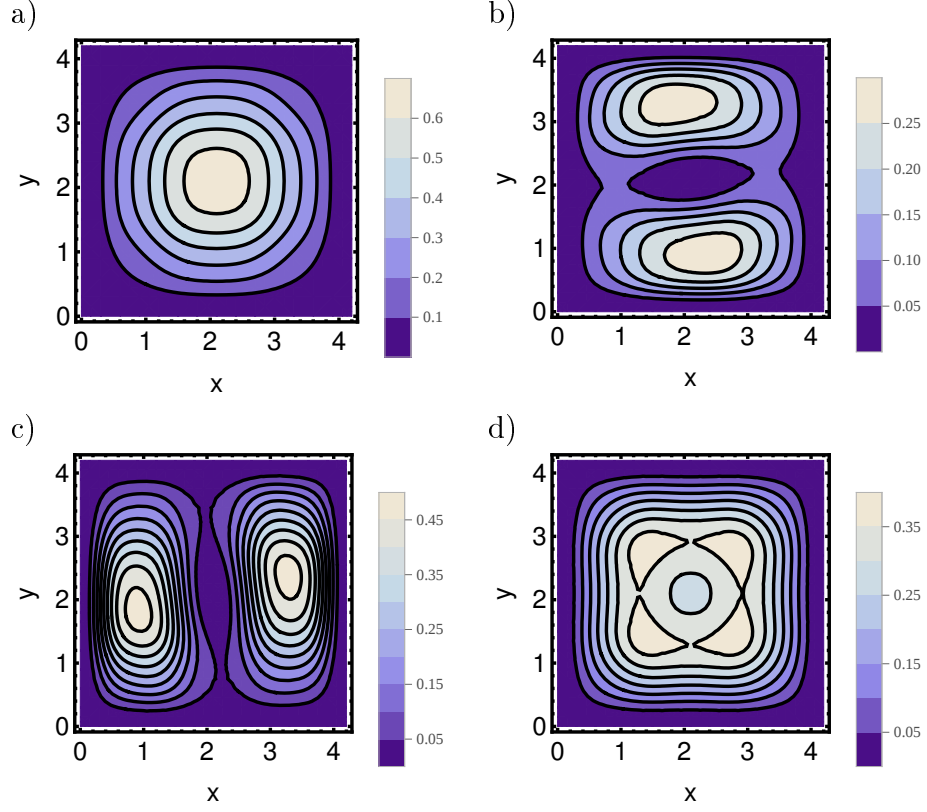


Figure 2.3: Cross sections at $z = 2.1$ nm (center) of the envelope wave functions for the four lowest energy electron states for PbS nanocubes 4.2 nm in length. The four states have respective energies of (a) 0.47 eV, (b) 0.68 eV, (c) 0.68 eV and (d) 0.71 eV. Wave functions are plotted in terms of $|\mathcal{F}(\mathbf{r})|^2$, which sums over contributions from all four components.

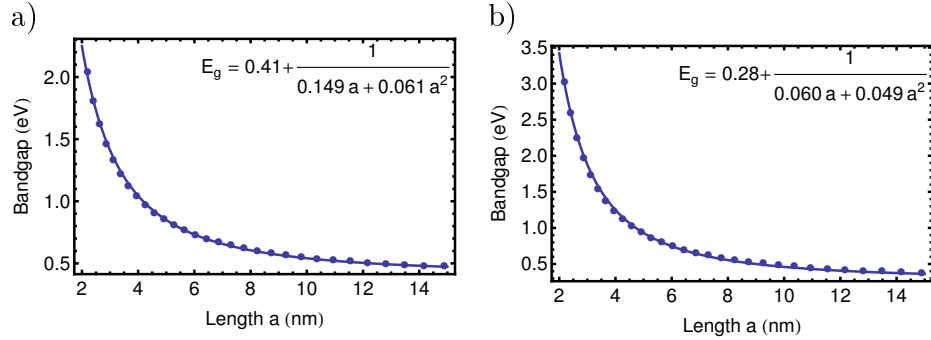


Figure 2.4: (a) Fitting of PbS cube bandgap with an analytic expression. (b) Fitting of PbSe cube bandgap with an analytic expression.

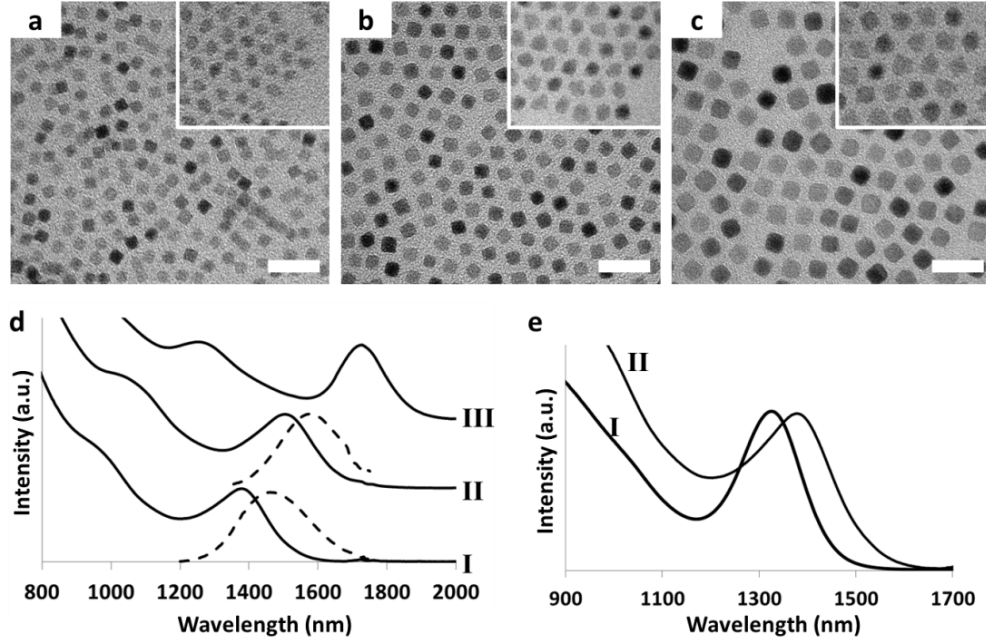


Figure 2.5: (a-c) TEM images of cubic PbS NCs of different sizes (edge): a, 4.6 ± 0.3 nm; b, 5.5 ± 0.3 nm; c, 7.0 ± 0.4 nm. Insets of a-c are TEM images of the corresponding starting quasi-spherical PbS NCs with sizes (diameter): a, 5.2 ± 0.4 nm; b, 5.9 ± 0.4 nm; c, 7.3 ± 0.4 nm. The inset and main pictures have the same magnification. Scale bar: 20 nm. (d) Optical absorption (solid) and photoluminescence (dashed) spectra of the same cubic PbS NCs: I, 4.6 nm; II, 5.5 nm; III, 7.0 nm. (e) Optical absorption spectra of 4.6 nm cubic PbS NCs (II) and their starting quasi-spherical PbS NCs (I).

smaller than the diameters of the original NCs. Figure 2.5d shows a nice progression of their absorption and photoluminescence peaks position of these nanocubes. Figure 2.5e shows slightly broader first exciton peak, indicating that the size monodispersity is a little bit worse than the original particles.

Figure 2.6 compares the measured 1st and 2nd absorption peaks with the calculated transition energy from $(111)_h$ to $(111)_e$ and $(112)_h$ to $(112)_e$. Transitions from $(111)_h$ to $(112)_e$ and $(112)_h$ to $(111)_e$ are parity-forbidden. The theory agrees well with the experimental data. This indicates that the newly added corners of the nanocubes are indeed integrated into the NC, with no defects or crystal

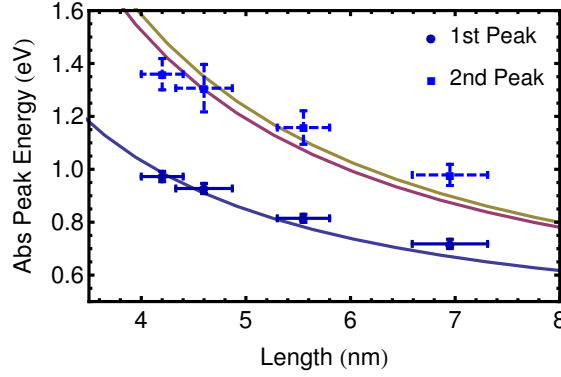


Figure 2.6: Calculated transition energy from $(111)_h$ to $(111)_e$ and $(112)_h$ to $(112)_e$ compared with measured center positions of the first and second absorption peaks. The error bars for length are the standard deviations of the cube lengths measured in TEM. The error bars for peak energies are estimated as HWHM of the 2nd derivatives of the peaks in absorption spectra.

misalignment. This combined with the fact that we were also able to align these nanocubes very easily into simple cubic lattice, we believe that the future application of nanocubes in electronic devices is very promising.

2.4 Lead Sulfide Nanosheets

Anisotropically-shaped semiconductor nanostructures have the potential to achieve very efficient charge transport while maintaining quantum confinement, due to the possibility of separating the dimensions for transport and confinement. Indeed, early measurements of single colloiddally grown nanowires [28, 29] and nanosheets [30] showed higher mobility than assemblies of the corresponding nanocrystals (NCs). In addition, the lowest exciton transitions in nanowires and nanosheets can have giant oscillator strengths connected with coherent center-of-mass motion.[31, 18] Combined with the high density of states near the energy gap and slow Auger recombination, nanosheets and nanowires have con-

sistently exhibited improved stimulated emission [32, 33] and multiple exciton generation,[34, 35, 36] thus showing promise for various optoelectronic device applications. Additional motivation to study nanosheets comes from the fact that they can be considered a limiting case of atomically-coherent nanocrystal superlattices [37, 38], which are sometimes referred to as having dimension slightly less than two.[39]

The rock salt crystal structure of the lead salts makes it difficult to colloiddally synthesize an anisotropically-shaped nanostructure. Schliehe *et al.* first synthesized thin lead sulfide nanosheets using two-dimensional oriented attachment.[40] Later, Acharya *et al.* reported a similar method, *via* collective coalescence of nanowires.[41] Very limited optical characterization of the structures was reported. Only recently, a few groups have reproduced and improved on Schliehe’s synthesis method,[42, 43] and reported absorption and fluorescence spectra of sheets with varying size.[36, 44]

Thanks to their highly anisotropic shape, the electronic structure of lead-salt nanosheets will be quite different from that of nanospheres or nanocubes, which are atomic-like. With strong quantum confinement in one direction (which we refer to as the vertical or z direction), but no quantum confinement in the lateral directions, energy bands form. The Coulomb interaction between charges will be mediated by the host environment, which generally has much smaller dielectric constant than the semiconductor. The reduction in screening of the Coulomb interaction compared to bulk material should yield tightly-bound excitons,[45, 46, 17, 47] similar to 1-D nanowires/nanorods,[17] and CdSe nanoplatelets.[47] Allan and Delerue reported tight-binding calculations of the electronic structure of PbSe nanosheets.[11] Their results show that the surfaces do not lead to states in the energy gap, and

predict that the energy gap varies inversely with the sheet thickness. On the other hand, they only calculate the single electron states, and did not include the coulomb interaction of the electron and hole in the sheet, which is an integral part of the exciton states.

To properly account for the strong Coulomb interaction, we separate the degrees of freedom into strongly confined vertical motion and Coulomb-coupled lateral motion. In the vertical direction quantum confinement dominates, and we solve the Schrödinger equation without the Coulomb interaction, which is subsequently treated as a perturbation. The resulting energy bands are the dispersion relations for electrons in the lateral directions. The Coulomb interaction between electron and hole is calculated using results from the electrostatic potential of a charge in an infinite slab of dielectric. This interaction is averaged over the vertical wave functions to obtain the equivalent two-dimensional (2D) Coulomb interaction. Finally, the motion in 2D is solved numerically to obtain the exciton binding energy. Results of the calculations will be compared with existing optical data.

2.4.1 Ansatz Solution in Vertical Direction

The boundary conditions for the nanosheet are assumed to be those of an infinite potential well,

$$\mathcal{F}(z = 0, d) = 0 \tag{2.9}$$

where d is the thickness of the nanosheet.

We define the vertical direction as the z direction. Given the translational

symmetry in the x-y plane, we take as an *ansatz*

$$F_j(r) = \sum_{\alpha=1}^{\infty} A_{j,\alpha} e^{ik_x x} e^{ik_y y} \sin \frac{\alpha \pi z}{d}, \quad j = 1 \dots 4 \quad (2.10)$$

Substituting Eq. 2.10 into the Schrödinger equation (Eq. 2.2), and using the orthogonality relations Eq. 2.5a, 2.5b yields four groups of coupled linear equations

$$\frac{4\hbar P}{md} i \left(-\sum'_{\alpha} \frac{\alpha \cdot \alpha_0}{\alpha_0^2 - \alpha^2} A_{3,\alpha} \right) + \frac{\hbar P}{m} (k_x - ik_y) A_{4,\alpha_0} = \left(E - \frac{E_g}{2} - \frac{\hbar^2}{2m^-} \left(k_x^2 + k_y^2 + \left(\frac{\alpha_0 \pi}{d} \right)^2 \right) \right) A_{1,\alpha_0} \quad (2.11a)$$

$$\frac{4\hbar P}{md} i \left(\sum'_{\alpha} \frac{\alpha \cdot \alpha_0}{\alpha_0^2 - \alpha^2} A_{4,\alpha} \right) + \frac{\hbar P}{m} (k_x + ik_y) A_{3,\alpha_0} = \left(E - \frac{E_g}{2} - \frac{\hbar^2}{2m^-} \left(k_x^2 + k_y^2 + \left(\frac{\alpha_0 \pi}{d} \right)^2 \right) \right) A_{2,\alpha_0} \quad (2.11b)$$

$$\frac{4\hbar P}{md} i \left(-\sum'_{\alpha} \frac{\alpha \cdot \alpha_0}{\alpha_0^2 - \alpha^2} A_{1,\alpha} \right) + \frac{\hbar P}{m} (k_x - ik_y) A_{2,\alpha_0} = \left(E + \frac{E_g}{2} + \frac{\hbar^2}{2m^+} \left(k_x^2 + k_y^2 + \left(\frac{\alpha_0 \pi}{d} \right)^2 \right) \right) A_{3,\alpha_0} \quad (2.11c)$$

$$\frac{4\hbar P}{md} i \left(\sum'_{\alpha} \frac{\alpha \cdot \alpha_0}{\alpha_0^2 - \alpha^2} A_{2,\alpha} \right) + \frac{\hbar P}{m} (k_x + ik_y) A_{1,\alpha_0} = \left(E + \frac{E_g}{2} + \frac{\hbar^2}{2m^+} \left(k_x^2 + k_y^2 + \left(\frac{\alpha_0 \pi}{d} \right)^2 \right) \right) A_{4,\alpha_0} \quad (2.11d)$$

The sums run over all terms (indexed by α) that have parity opposite that of α_0 . The electron states are calculated with a finite number of terms, $\alpha \leq N = 16$. The resulting fractional error in the energy gap is estimated as $< 0.1\%$.

Example results are presented for a 3-nm PbS nanosheet. The energies of the first 12 states at $k_x = k_y = 0$ are plotted in Figure 2.7a. The calculated energy levels are consistent with our expectation of quantum confinement in one dimension. All states are doubly degenerate with spin. Plotting the energies as functions of the lateral momentum $(k_{x,y})$ yields the dispersion relation of electrons in the 2D plane (Figure 2.7b). We fit the energies to a parabolic function $E_n(k_{x,y}) = \frac{\hbar^2 k_{x,y}^2}{2m_{eff,n}}$, assuming that the dispersion relation at small $k_{x,y}$ is described by a simple one-band effective mass model. The fits are very good for $k_{x,y} \lesssim 0.4 \text{ nm}^{-1}$. Above that, the energy deviates from the simple parabolic model, particularly for the e_1

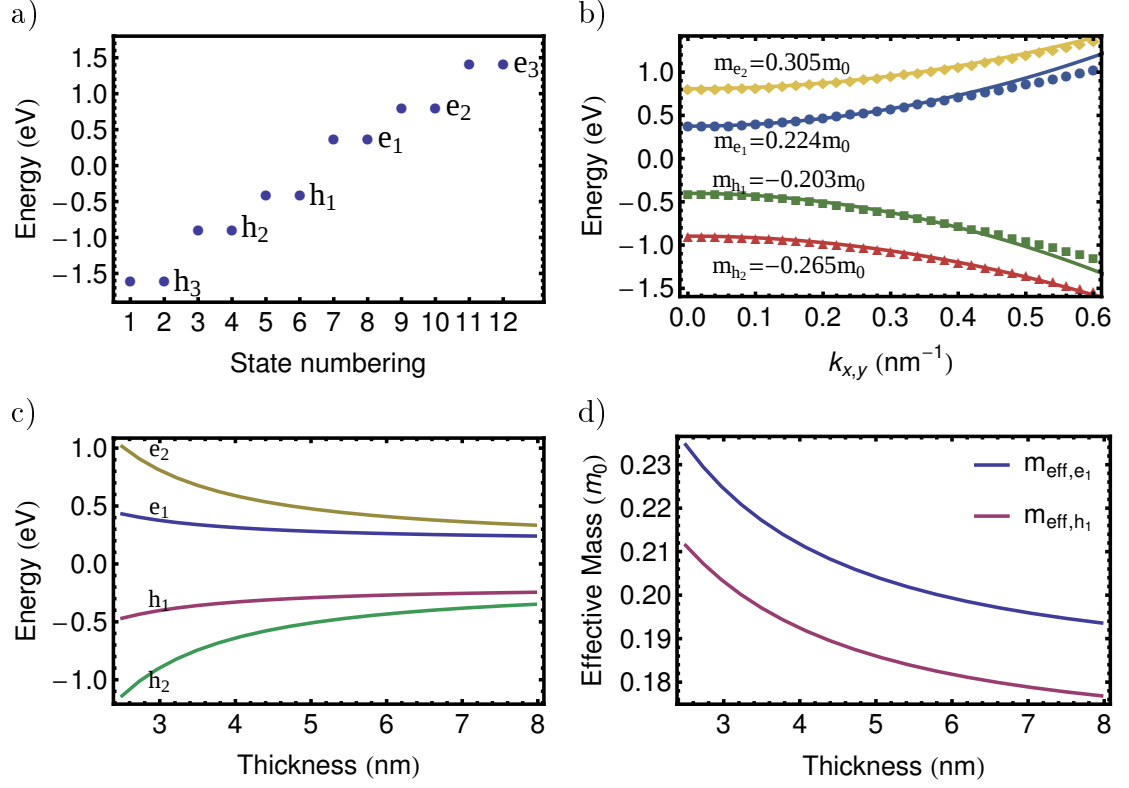


Figure 2.7: (a) Energies for 12 states close to the energy gap for a 3-nm PbS nanosheet. (b) Energy of electron with different lateral momentum $k_{x,y}$. The band structure in the x,y plane is isotropic. Lines are parabolic fits, with inferred effective masses indicated. (c) Energy levels and (d) 2D effective masses of PbS nanosheets of different thicknesses.

and h_1 bands. Figures 2.7c,d shows the thickness dependence of the energies and effective masses for different bands. With increasing thickness, the energy gaps and effective masses approach their bulk values.

2.4.2 Coulomb Interaction

The potential of a point charge in an infinite dielectric slab can be found by the method of images.[48] For a slab with dielectric constant ϵ_2 embedded in medium with dielectric constant ϵ_1 , the electric potential within the slab at any point (z, ρ)

in cylindrical coordinates due to a point charge q at the origin is

$$\begin{aligned}
U(z, \rho; a, b) = & f(z, \rho) + U_{image}(z, \rho; a, b) = f(z, \rho) \\
& + \sum_{n=0}^{\infty} \beta^{2n+1} f(z - 2an - 2b(n+1)) + \sum_{n=0}^{\infty} \beta^{2n+2} f(z - 2(a+b)(n+1)) \\
& + \sum_{n=0}^{\infty} \beta^{2n+1} f(z + 2bn + 2a(n+1)) + \sum_{n=0}^{\infty} \beta^{2n+2} f(z + 2(a+b)(n+1)) \quad (2.12)
\end{aligned}$$

where a and b are the distances from the point charge to the dielectric interfaces, $f(z, \rho) = \frac{1}{4\pi\epsilon_2} \frac{q}{\sqrt{z^2 + \rho^2}}$ is the electric potential of one charge q in the semiconductor with dielectric constant ϵ_2 , and $\beta = \frac{\epsilon_2 - \epsilon_1}{\epsilon_1 + \epsilon_2} > 0$. This result is more rigorously proven by directly solving the Laplace's equation. (see Appendix 2.6.1) Eq. 2.12 can be rewritten in a coordinate system with the origin shifted to one dielectric interface and in terms of the sheet thickness d ,

$$V(z_1, z_2, \rho) = U(z = z_2 - z_1, \rho; a = z_1, b = d - z_1). \quad (2.13)$$

First, we consider the self-interaction of a point charge with its image charges at the interfaces. For a charge q embedded in the medium at position $(z, 0)$, the electric potential at the same point is $V(z, z, 0)$. The energy of the electric field stored in the medium is $\frac{1}{2}qV(z, z, 0)$. The contribution from the first term in Eq. 2.12, $\frac{1}{2}qf(0, 0)$, is the energy of a bare charge embedded in an infinite medium. This energy is already accounted for in the work function of the semiconductor. The rest of the terms $\frac{1}{2}qV_{image}(z, z, 0)$ account for the energy of the interaction between the charge and its polarized charges at the dielectric interface, or the interface polarization energy. Figure 2.8a shows the shape of this potential energy for an electron(or hole) placed at position z . Due to the smaller dielectric constant in the host medium, this potential pushes the electron away from the interface, so it is called the dielectric confinement energy. The first-order correction to the

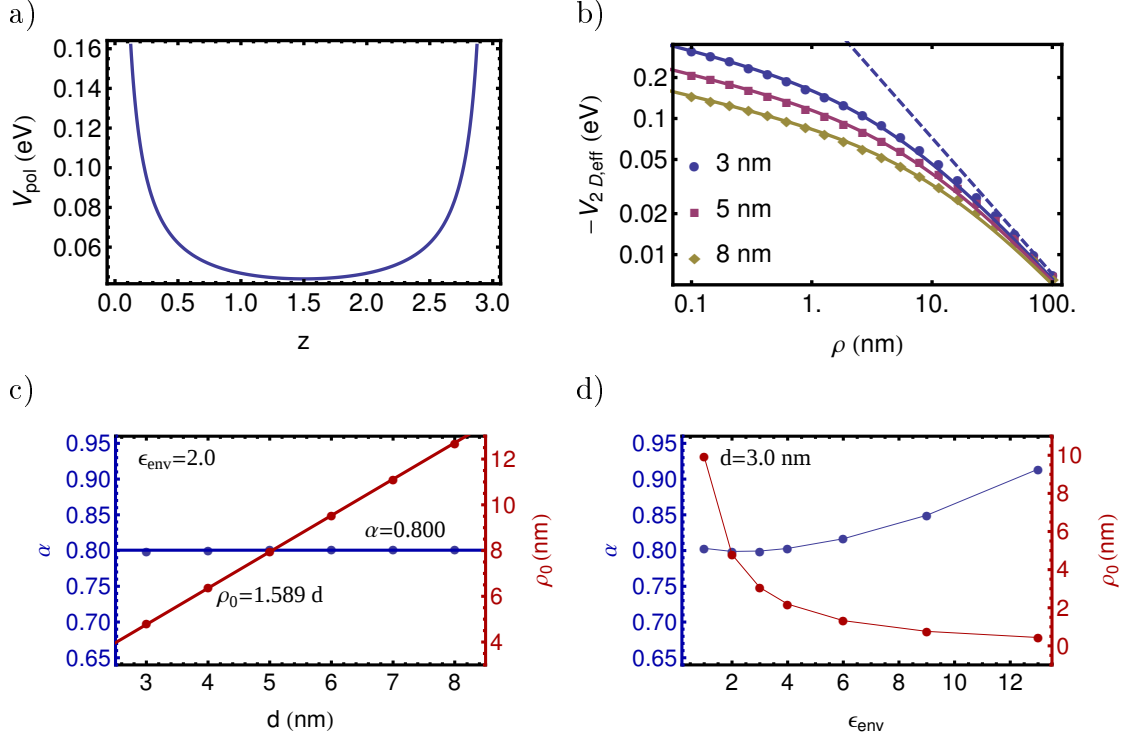


Figure 2.8: (a) Interface polarization energy potential of a 3-nm PbS nanosheet. Parameters: $\epsilon_1 = \epsilon_{env} = 2.0$, $\epsilon_2 = \epsilon_{PbS} = 17.0$. (b) Electron-hole Coulomb energy, averaged over the vertical wave functions of the lowest energy electron and hole bands for PbS nanosheets of indicated thickness. The solid curves are fits to the model potential $V_{2D,eff}(\rho) = -\frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho} \frac{1}{1+(\rho_0/\rho)^\alpha}$. The dashed curve corresponds to the Coulomb interaction with $\epsilon = \epsilon_{env}$, without the interfaces. (c) Fitting parameters α (blue) and ρ_0 (red) for the effective 2D potential for different thicknesses. α is consistently around 0.8, and ρ_0 is proportional to the thickness. (d) Dependence of fitting parameters α and ρ_0 for the effective 2D potential with dielectric constant of the environment.

energy of an electron due to the interface polarization energy is

$$V_{pol} = \int dz |\mathcal{F}_{e_1}(z)|^2 \frac{1}{2} q V_{image}(z, z, 0) \quad (2.14)$$

The polarization energy of the electron and hole are both 51 meV, for a total of 102 meV, in 3-nm PbS nanosheets.

The 2D effective Coulomb potential between an electron and a hole in the

lowest energy bands is

$$V_{2D,eff}(\rho) = \iint dz_e |\mathcal{F}_{e1}(z_e)|^2 dz_h |\mathcal{F}_{h1}(z_h)|^2 (-V(z_h, z_e, \rho)). \quad (2.15)$$

Here we neglect the exchange interaction, which is much smaller than the direct Coulomb interaction.[49, 50] The negative sign is due to the opposite charges. The 2D Coulomb potentials for 3-nm, 5-nm and 8-nm PbS nanosheets are plotted in Figure 2.8b as the dots. Thinner nanosheets produce stronger Coulomb interactions.

The 2D effective Coulomb potential has the limit $\lim_{\rho \rightarrow \infty} V_{2D,eff}(\rho) = -\frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho}$, so it approaches the direct Coulomb interaction mediated by the dielectric constant of the environment, ϵ_1 (dashed curve in Figure 2.8b). For small ρ , the 2D Coulomb potential approaches another power law with exponent smaller than 1. We fit the effective 2D Coulomb potential to an analytic form (solid curves in Figure 2.8b)

$$V_{2D,eff}(\rho) = -\frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho} \frac{1}{1 + (\rho_0/\rho)^\alpha} \quad (2.16)$$

which goes to the correct limiting forms

$$\lim_{\rho \rightarrow 0} V_{2D,eff}(\rho) = -\frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho_0^\alpha} \rho^{-(1-\alpha)} \quad (2.17a)$$

$$\lim_{\rho \rightarrow \infty} V_{2D,eff}(\rho) = -\frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho} \quad (2.17b)$$

, with ρ_0 the transition point from one limit to the other. For a fixed medium dielectric constant of 2.0, the best-fit value for α is consistently 0.80, while ρ_0 is proportional to the sheet thickness; for fixed thickness at 3 nm, with increasing medium dielectric constant, the interface dielectric effect gets weaker, and α increases slightly while ρ_0 decreases (Figure 2.8c,d).

2.4.3 2D Lateral Motion and Exciton Formation

Last, we solve for the lateral motion of the electron and hole in the effective 2D Coulomb potential. The Schrödinger equation is

$$\left[-\frac{\hbar^2}{2m_{e1}} \frac{\partial^2}{\partial \mathbf{r}_e^2} - \frac{\hbar^2}{2m_{h1}} \frac{\partial^2}{\partial \mathbf{r}_h^2} + V_{2D,eff}(\mathbf{r}_h - \mathbf{r}_e) \right] \Psi(\mathbf{r}_e, \mathbf{r}_h) = E \Psi(\mathbf{r}_e, \mathbf{r}_h) \quad (2.18)$$

The motion can be separated into the center of mass motion and the relative motion $\Psi(\mathbf{r}, \mathbf{R}) = \Psi_{cm}(\mathbf{R}) \psi_{rel}(\mathbf{r})$, where the center of mass wave function $\Psi_{cm}(\mathbf{R})$ is a plane wave. Since the interaction is also independent of the relative direction, the relative motion can be further separated as $\psi_{rel}(\rho, \phi) = R(\rho) \Phi(\phi)$, where $\Phi(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$, with orbital angular momentum perpendicular to the sheet $m\hbar$. The equation for the radial wave function $R(\rho)$ becomes

$$\frac{d^2}{d\rho^2} R(\rho) + \frac{1}{\rho} \frac{d}{d\rho} R(\rho) + \left[\frac{2\mu}{\hbar^2} \left(E_{rel} + \frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho} \frac{1}{1 + (\rho_0/\rho)^\alpha} \right) - \frac{m^2}{\rho^2} \right] R(\rho) = 0 \quad (2.19)$$

where $\mu = \frac{m_{e1} m_{h1}}{m_{e1} + m_{h1}}$ is the reduced mass, and the analytic form of the 2D Coulomb interaction (Eq.2.16) is included. Eq.2.19 is solved numerically (see Appendix 2.6.2 for details). Figure 2.9a shows the energy levels for the first few bonding states. The binding energy for the lowest energy exciton in a 3-nm PbS nanosheet is 83 meV. The radial wave functions for the first four lowest energy states are plotted in Figure 2.9b.

Figure 2.10a summarizes the self energies (calculated with Eq.2.14), the exciton binding energy, and the total energy with varying sheet thicknesses. Figure 2.10b summarizes the same quantities but for varying dielectric constant of the environment. The exciton binding energy partially cancels out the self polarization energy, and as a result, the total energy shift due to Coulomb interaction is much smaller than either one. Figures 2.10c,d show the average distance between the electron and hole $\langle \rho \rangle$ for the lowest exciton state. The exciton size is on the order of a few

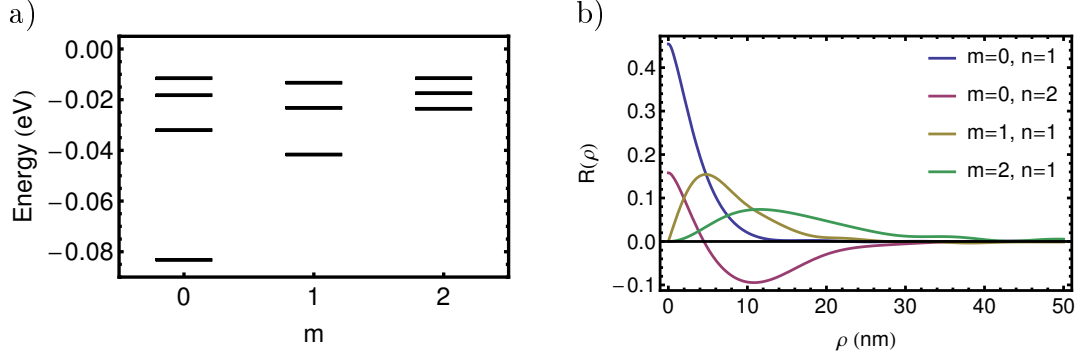


Figure 2.9: (a) First few exciton energies for $m = 0, 1, 2$. (b) Radial wave functions for the four lowest energy states. Material: PbS, 3 nm.

nm and increases roughly linearly with the sheet thickness and quadratically with the medium dielectric constant.

2.4.4 Interband Optical Transition Dipoles

To compare the results with the absorption spectrum, we calculate the oscillator strength of the interband optical transition dipoles for lead salt nanosheets. The oscillator strength is proportional to the square of the dipole operator, which can be written as [2]

$$\begin{aligned}
 M_{c,v} &= |\langle \Psi_c(\mathbf{r}) | \mathbf{e} \cdot \mathbf{p} | \Psi_v(\mathbf{r}) \rangle|^2 \\
 &= \left| (\hat{e}_{field} \cdot \hat{e}_{valley}) P_l \int d\mathbf{r} \mathcal{F}_{e_{n1}}^\dagger(\mathbf{r}) (\sigma_x \otimes \sigma_z) \mathcal{F}_{h_{n2}}(\mathbf{r}) \right|^2 \\
 &= (\hat{e}_{field} \cdot \hat{e}_{valley})^2 P_l^2 \left| \int dz \mathcal{F}_{e_{n1}}^\dagger(z) (\sigma_x \otimes \sigma_z) \mathcal{F}_{h_{n2}}(z) \right|^2 \left| \int d\boldsymbol{\rho} F_{e_{n1}}^\dagger(\boldsymbol{\rho}) F_{h_{n2}}(\boldsymbol{\rho}) \right|^2
 \end{aligned}$$

where we only keep the largest dipole moment contributed by the Bloch functions, and we also separate the vertical and lateral envelope wave functions. P_l is the longitudinal Kane momentum-matrix element between the conduction and valence band-edge Bloch functions.

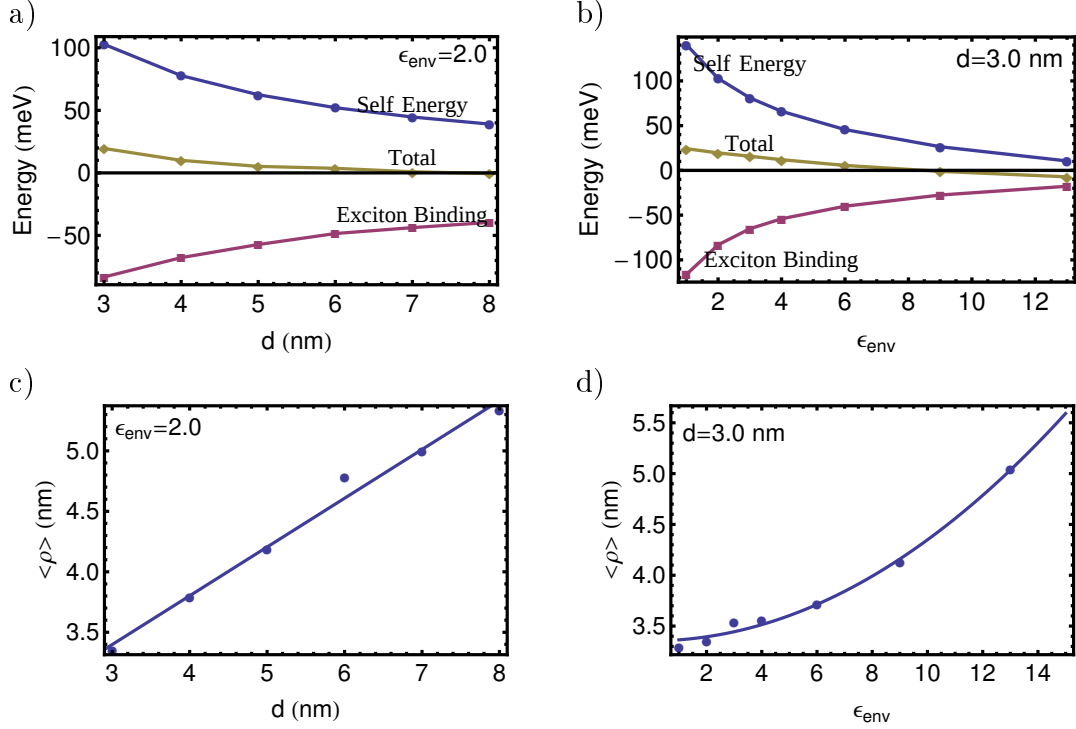


Figure 2.10: (a,b) Interface polarization energy (electron plus hole), exciton binding energy, and total energy and (c,d) average electron and hole distance $\langle \rho \rangle$ for the lowest exciton state ($m=0$, $n=1$), for (a,c) different thickness, assuming $\epsilon_{env} = 2.0$ and (b,d) different dielectric constant for the medium, assuming thickness $d = 3.0$ nm.

The term $\left| \int dz \mathcal{F}_{e_{n1}}^\dagger(z) (\sigma_x \otimes \sigma_z) \mathcal{F}_{h_{n2}}(z) \right|^2$ determines the selection rules of optical transitions between different subbands. As a consequence of the inversion symmetry, only transitions with $n1$ and $n2$ of the same parity are allowed, and the strongest transitions have $n1 = n2$.

The term $\left| \int d\rho F_c^\dagger(\rho) F_v(\rho) \right|^2$ is the overlap integral of the electron and hole lateral wave functions. Due to the negligible photon momentum compared with electron momentum, optical transitions from the ground state will be allowed only if the center of mass momentum of the exciton is zero. Thus in the center of mass coordinate, the overlap integral is reduced to $|R_{m,n}(r=0)|^2$. [51] This has the consequence that direct transitions only create excitons states with $m = 0$. All

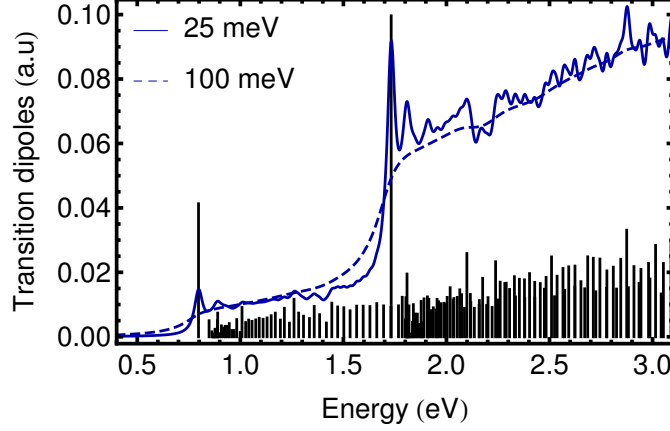


Figure 2.11: Interband optical transition dipoles of 3-nm PbS nanosheets. The solid line is the absorption spectrum calculated assuming broadening $\delta = 25$ meV; the dashed line corresponds to $\delta = 100$ meV.

other transitions are forbidden.

Figure 2.11 shows the transition dipoles calculated for 3-nm PbS nanosheets. The transition band that starts near 0.8 eV is the $h_1 \rightarrow e_1$ transition; the second band that starts near 1.75 eV is the $h_2 \rightarrow e_2$ transition. The lowest-energy exciton carries the largest dipole moment. We can calculate the linear optical susceptibility

$$\chi(\omega) \propto \sum_{n1,n2} \left| \int dz \mathcal{F}_{e_{n1}}^\dagger(z) (\sigma_x \otimes \sigma_z) \mathcal{F}_{h_{n2}}(z) \right|^2 \sum_n \frac{\left| R_n^{(n1,n2)}(r=0) \right|^2}{E_n^{(n1,n2)} - \omega - i\delta}$$

and the absorption coefficient $\alpha(\omega) = 4\pi\omega / (cn(\omega)) \text{Im}[\chi(\omega)]$. The absorption spectra of 3-nm PbS nanosheets with $\delta = 25$ meV and $\delta = 100$ meV are plotted in Figure 2.11. When the broadening (which includes homogenous and inhomogenous broadening) is smaller than the exciton binding energy, the first exciton peak is visible (in the case of $\delta = 25$ meV), similar to the case of high quality cadmium-salt nanoplatelets.[18] Otherwise, only an indistinct step is observed ($\delta = 100$ meV).

2.4.5 Lead Selenide Nanosheets

The electronic states of lead selenide nanosheets are calculated using exactly the same method. The results are summarized in Figure 2.12 for reference. Band parameters used are from the literature.[17]

2.4.6 Comparison with Experiments

Experimental data on the size-dependent optical properties of lead-salt nanosheets is currently quite limited, due to challenges in the synthesis of high-quality samples and reliable measurements of the thickness. Ideally, the thickness can be measured directly with an atomic-force microscope.[36, 44] However, the organic ligands on the surfaces will obscure the measurement, and special surface treatments to strip off these ligands are needed for reliable measurement. The thickness can also be estimated by applying the Scherrer analysis to the linewidths in the x-ray diffraction pattern.[40, 36] However, nanosheet thicknesses are generally not uniform, and this inhomogeneous broadening naturally complicates the analysis. On the other hand, owing to the 2D electronic structure, the optical absorption spectra of nanosheets will have much less prominent absorption peaks than 1D or 0D nanocrystals, which makes it also harder to determine the exact position of the optical bandgap.[44] The scattering background is also larger due to the micro lateral size. We plot all the available data in the literature on size-dependent optical bandgap in Figure 2.13a. Our model (solid line) agrees reasonably well with available data, but better control of the synthesis and more systematic study of the size-dependent optical properties are sorely needed. The calculated optical bandgap of PbSe nanosheets is shown in Figure 2.13b for reference. To our knowl-

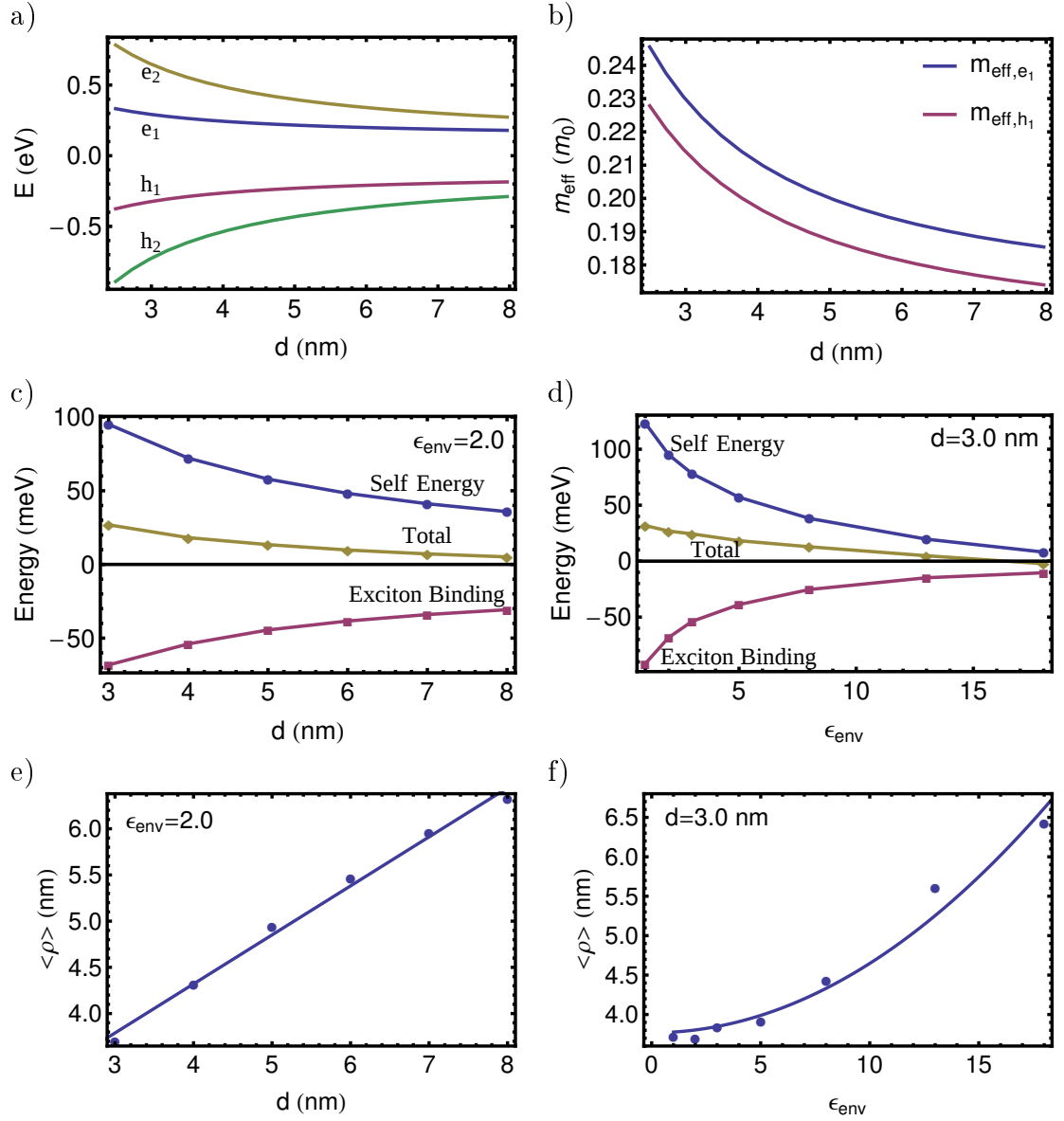


Figure 2.12: Summary of results for lead selenide nanosheets. (a) 2D band energies without Coulomb interaction. (b) 2D effective mass. (c,e) Self polarization energy and exciton binding energy, and exciton size as a function of thickness. (d,f) Same quantities as a function of medium dielectric constant.

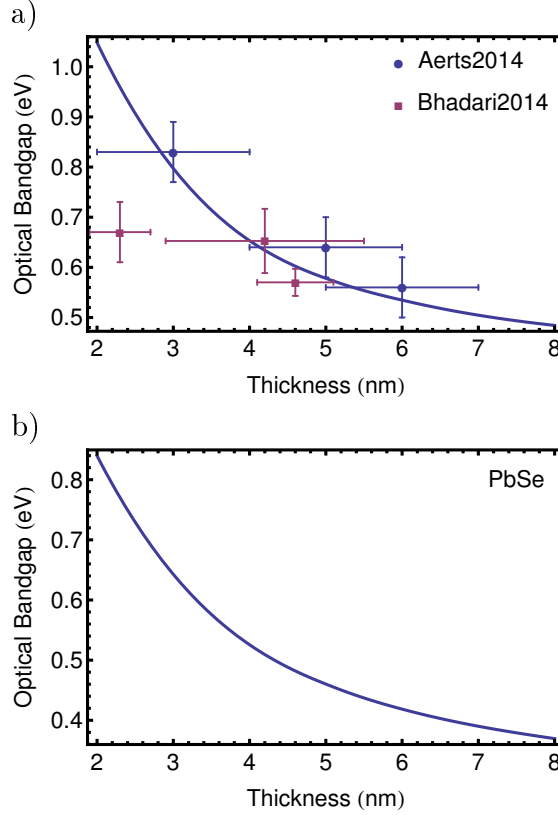


Figure 2.13: (a) Optical bandgap for PbS nanosheets. Solid line is the 4-band model result, corrected by Coulomb interaction. Data points are collected from literatures. (b) Optical bandgap for PbSe nanosheets.

edge, there is no report of successful synthesis of strongly confined PbSe nanosheets yet.

2.4.7 Discussion and Conclusion

The assumed separation of the electron motion into vertical and lateral motions requires that the energy difference between subbands be much larger than the binding energy of the exciton. The subband separation energy ranges from 400 meV to 100 meV for 3-nm to 8-nm PbS or PbSe nanosheets. The binding energy ranges from 80 meV to 30 meV over the same range of sizes. Therefore, the

approximation is reasonable for this size range. For much thicker nanosheets, coupling between subbands due to the Coulomb interaction will be too large to be treated as a perturbation.

For colloidal PbS or PbSe nanosheets in common organic solvents, the exciton binding energy is between 30 and 80 meV, depending on the size. This energy is larger than the thermal energy at room temperature. This indicates that at room temperature, the electron and hole in the nanosheets are tightly bound, and move as a single entity within the lateral dimension. Thus, if inhomogeneous broadening is small enough (such as measurement on a single sheet of uniform thickness), one should observe the exciton peak above the flat plateau in the absorption spectrum.

On the other hand, compared with 1D lead salt nanowires with the same diameter, the exciton binding energy is a lot smaller. Three major effects are responsible. First, in general, lower-dimensional excitons have larger binding energies than those in higher dimensions. Second, since the electron and hole are only confined in one direction, they are relatively more spread out than the electron and hole in a nanowire. This reduces the effective Coulomb interaction, especially at short distances. Third, the dielectric screening is stronger in 2D, and this also decreases the Coulomb interaction, especially at long distances.

Due to the stronger Coulomb interaction, processes that are Coulomb mediated such as multiple exciton recombination,[52] and carrier multiplication will likely be enhanced,[36] compared with 0D or 3D structures. Also, due to the exciton formation, the multiple exciton recombination will likely be a bimolecular recombination instead of three particle interaction, which change the scaling of the recombination rate as a function of carrier density from n^3 to n^2 .

2.5 Conclusion

In this chapter, we presented the basic methodology of calculating the electronic structure in a quantum confined nanocrystal. We illustrated the method by calculating the electronic states of lead sulfide nanocubes and nanosheets and compared them with experiments. In the case of nanosheets, due to its highly anisotropic shape, the coulomb interaction was calculated in a nonperturbative way in the lateral dimension. The exciton binding energies are generally larger than the thermal energy at room temperature, and the electron and hole form tightly bound excitons and move together in the lateral dimensions.

2.6 Appendix

2.6.1 Electric Potential of a Point Charge Embedded in a Dielectric Slab

The method used is presented in [53]. We set the center of the coordinate to be at the original charge q , z axis to be perpendicular to the interface and ρ axis to be parallel to the interface. The entire system is symmetric with respect to rotation along the z axis. (Figure 2.14). The distance from the point charge to one interface is a and to the other is b .

In the dielectric medium ϵ_2 ($-a < z < b$), the potential due to the point charge alone is

$$V = \frac{q}{4\pi\epsilon_2 r} = \frac{q}{4\pi\epsilon_2} \int_0^\infty J_0(k\rho) e^{-k|z|} dk \quad (2.20)$$

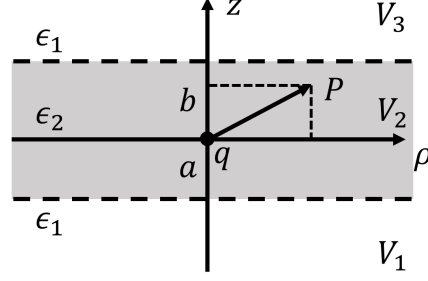


Figure 2.14: Schematic of calculating electric potential. ϵ_1 is the dielectric constant of the environment. ϵ_2 is the dielectric constant of the semiconductor. The origin of the coordinate is set at the free charge q .

Since this is a solution of Laplace's equation, which involves z and ρ only, we shall still have a solution if we insert any function of k under the integral sign. Let V_2 be the potential in the dielectric slab ($-a < z < b$), then

$$V_2 = \frac{q}{4\pi\epsilon_2} \left(\int_0^\infty J_0(k\rho) e^{-k|z|} dk + \int_0^\infty \Phi(k) J_0(k\rho) e^{kz} dk + \int_0^\infty \Psi(k) J_0(k\rho) e^{-kz} dk \right) \quad (2.21)$$

The second and third terms represent the potential due to the polarization at the interfaces. In the region $z < -a$, there are no free charges, and the potential V_1 can be written as

$$V_1 = \frac{q}{4\pi\epsilon_2} \int_0^\infty \Theta(k) J_0(k\rho) e^{kz} dk \quad (2.22)$$

Similarly, V_3 can be written as

$$V_3 = \frac{q}{4\pi\epsilon_2} \int_0^\infty \Omega(k) J_0(k\rho) e^{-kz} dk \quad (2.23)$$

To determine $\Phi(k)$, $\Psi(k)$, $\Theta(k)$ and $\Omega(k)$, we use the boundary conditions

$$V_1|_{z=-a} = V_2|_{z=-a} \quad (2.24a)$$

$$\epsilon_1 \frac{\partial V_1}{\partial z} \Big|_{z=-a} = \epsilon_2 \frac{\partial V_2}{\partial z} \Big|_{z=-a} \quad (2.24b)$$

$$V_2|_{z=b} = V_3|_{z=b} \quad (2.24c)$$

$$\epsilon_2 \frac{\partial V_2}{\partial z} \Big|_{z=b} = \epsilon_1 \frac{\partial V_3}{\partial z} \Big|_{z=b} \quad (2.24d)$$

Before we actually plug in the forms Eq.2.21, 2.22, 2.23, we notice that if we have

$$\int_0^\infty f_1(k) J_0(k\rho) dk = \int_0^\infty f_2(k) J_0(k\rho) dk \quad (2.25)$$

then we have $f_1(k) = f_2(k)$ for an arbitrary k . Thus it is easy to show the boundary conditions evaluates to

$$\Theta(k) e^{-ka} = e^{-ka} + \Phi(k) e^{-ka} + \Psi(k) e^{ka} \quad (2.26a)$$

$$k\Theta(k) e^{-ka} = \epsilon_r (k e^{-ka} + k\Phi(k) e^{-ka} - k\Psi(k) e^{ka}) \quad (2.26b)$$

$$\Omega(k) e^{-kb} = e^{-kb} + \Phi(k) e^{kb} + \Psi(k) e^{-kb} \quad (2.26c)$$

$$-k\Omega(k) e^{-kb} = \epsilon_r (-k e^{-kb} + k\Phi(k) e^{kb} - k\Psi(k) e^{-kb}) \quad (2.26d)$$

where $\epsilon_r = \epsilon_2/\epsilon_1$. Solving $\Phi(k)$ and $\Psi(k)$ and we get

$$\Phi(k) = \frac{\beta (\beta + e^{2ka})}{-\beta^2 + e^{2(a+b)k}} \quad (2.27a)$$

$$\Psi(k) = \frac{\beta (\beta + e^{2kb})}{-\beta^2 + e^{2(a+b)k}} \quad (2.27b)$$

where $\beta = \frac{\epsilon_r - 1}{\epsilon_r + 1} = \frac{\epsilon_2 - \epsilon_1}{\epsilon_1 + \epsilon_2}$. We can rewrite the denominator in Taylor expansion as

$$\begin{aligned} \frac{1}{-\beta^2 + e^{2(a+b)k}} &= e^{-2(a+b)k} \sum_{n=0}^{\infty} (\beta^2 e^{-2(a+b)k})^n \\ &= \sum_{n=0}^{\infty} \beta^{2n} \cdot e^{-2(a+b)k(n+1)} \end{aligned} \quad (2.28)$$

Putting these all back into Eq.2.21, we obtain

$$\begin{aligned}
V_2 &= \frac{q}{4\pi\epsilon_2} \int_0^\infty J_0(k\rho) e^{-k|z|} dk \\
&\quad + \frac{q}{4\pi\epsilon_2} \int_0^\infty J_0(k\rho) \sum_{n=0}^\infty \beta^{2n+2} e^{-2(a+b)(n+1)k} e^{kz} dk \\
&\quad + \frac{q}{4\pi\epsilon_2} \int_0^\infty J_0(k\rho) \sum_{n=0}^\infty \beta^{2n+1} e^{-(2an+2b(n+1))k} e^{kz} dk \\
&\quad + \frac{q}{4\pi\epsilon_2} \int_0^\infty J_0(k\rho) \sum_{n=0}^\infty \beta^{2n+2} e^{-2(a+b)(n+1)k} e^{-kz} dk \\
&\quad + \frac{q}{4\pi\epsilon_2} \int_0^\infty J_0(k\rho) \sum_{n=0}^\infty \beta^{2n+1} e^{-(2bn+2a(n+1))k} e^{-kz} dk \\
&= \frac{q}{4\pi\epsilon_2} \frac{1}{\sqrt{z^2 + \rho^2}} \\
&\quad + \frac{q}{4\pi\epsilon_2} \sum_{n=0}^\infty \beta^{2n+2} \frac{1}{\sqrt{(z - 2(a+b)(n+1))^2 + \rho^2}} \\
&\quad + \frac{q}{4\pi\epsilon_2} \sum_{n=0}^\infty \beta^{2n+1} \frac{1}{\sqrt{(z - 2an - 2b(n+1))^2 + \rho^2}} \\
&\quad + \frac{q}{4\pi\epsilon_2} \sum_{n=0}^\infty \beta^{2n+2} \frac{1}{\sqrt{(z + 2(a+b)(n+1))^2 + \rho^2}} \\
&\quad + \frac{q}{4\pi\epsilon_2} \sum_{n=0}^\infty \beta^{2n+1} \frac{1}{\sqrt{(z + 2bn + 2a(n+1))^2 + \rho^2}} \tag{2.29}
\end{aligned}$$

where we used Eq.2.20 in reverse. One can easily verify that the result here is equivalent to result 2.12 obtained using the image method.

2.6.2 Numerical Calculation of the Radial Wave Functions

We solve Eq.2.19 numerically, by converting it into a discrete eigenvalue problem. First we impose a size limit, by assuming $0 \leq \rho \leq b$ and $R(\rho = b) = 0$, where b is

very large. Then we expand $R(\rho)$ in Fourier–Bessel series

$$R(\rho) = \sum_{n=1}^{\infty} c_n u_{m,n}(\rho) \quad (2.30)$$

where $u_{m,n}(\rho) = \frac{\sqrt{2}}{b} \frac{J_m(r_{m,n}\rho/b)}{J_{m+1}(r_{m,n})}$, $J_m(x)$ is Bessel function of the first kind, $r_{m,n}$ is the n th root of $J_m(x)$. Being Bessel functions, $u_{m,n}(\rho)$ satisfies

$$\left(\frac{d^2}{d\rho^2} + \frac{1}{\rho} \frac{d}{d\rho} - \frac{m^2}{\rho^2} \right) u_{m,n}(\rho) = - \left(\frac{r_{m,n}}{b} \right)^2 u_{m,n}(\rho) \quad (2.31a)$$

$$\int_0^b \rho d\rho u_{m,n}(\rho) u_{m,n'}(\rho) = \delta_{n,n'} \quad (2.31b)$$

Plugging Eqn 2.30 into Eqn 2.19, and using Bessel function properties, one obtains a set of discrete eigenvalue equations

$$\frac{\hbar^2}{2\mu} \left(\frac{r_{m,n}}{b} \right)^2 c_n + \sum_{n'=1}^{\infty} V_{m,n,n'} c_{n'} = E_{rel} c_n, \quad n = 1, 2, 3 \dots \quad (2.32)$$

where $V_{m,n,n'}$ is the integral of the Coulomb potential

$$V_{m,n,n'} = \int_0^b \rho d\rho \left(-\frac{1}{4\pi\epsilon_1} \frac{e^2}{\rho} \frac{1}{1 + (\rho_0/\rho)^\alpha} \right) u_{m,n}(\rho) u_{m,n'}(\rho) \quad (2.33)$$

We assume $b = 100$ nm, and use a cutoff $N = 200$ for the number of basis $1 \leq n, n' \leq N$, and calculate the energy and wave functions. Error for the exciton binding energy is estimated to be $< 1\%$.

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CHAPTER 3

DISORDER IN NANOCRYSTAL ASSEMBLIES

3.1 Introduction

Currently, one of the major goals in semiconductor nanocrystal solid research is to observe coherent transport of charge carriers. In an ordinary crystalline solid, atoms line up periodically to form a lattice. Instead of scattering the electrons, the interaction of the atoms with the electron forms an energy band. Ideally, the wave function of an electron in the band extends over the entire crystal, and electrons transport through these extended states. Typical semiconductors have carrier mobilities around $10^3 \text{ cm}^2/(\text{Vs})$ to $10^4 \text{ cm}^2/(\text{Vs})$.

For comparison, NC solids currently have mobilities that range from $10^{-3} \text{ cm}^2/(\text{Vs})$ to $10^1 \text{ cm}^2/(\text{Vs})$. [1, 2, 3, 4, 5, 6] The transport is usually attributed to nearest-neighbor or variable-range hopping. [7] Several studies have reported band-like transport, [8, 9, 10] based on observation of increased mobility with decreasing temperature. However, there has been controversy as to the real nature of the transport. It was shown [11] that even hopping transport can lead to a similar temperature dependence, and that alone cannot prove real transport through band-like states.

The fundamental limit for true band-like transport can be traced to the inherent disorder in a NC solids—that is, the energy disorder due to NC size inhomogeneity, and the coupling disorder due to imperfect alignment. Sufficient disorder leads to Anderson localization, [12, 13] the absence of delocalized states. Anderson localization has been extensively studied analytically, [14, 15] numerically, [16, 17, 18, 19, 20]

and experimentally.[21, 22, 23] Noriega *et al.* studied transport in organic semiconductors, and showed a strong correlation between paracrystallinity (structural disorder) in conjugated polymers and their charge transport efficiency.[24] Remacle *et al.* studied the effects of charging energy and disorder on charge transport in metal NC solids.[25] Artemyev *et al.* studied the existence of delocalized electron states in CdSe NC ensembles with different sizes and packing ratios.[26] However, the modeling of structural disorder in this work is not realistic enough to allow comparison with experiments.

In this chapter, we study numerically the criterion for band-like transport (i.e., carriers conduct through delocalized electronic states) in widely-investigated cadmium-salt and lead-salt NC solids. In section 3.2, we start from a Hamiltonian that explicitly models the on-site energy disorder and positional disorder realistically. We then use fractal dimension, which is the scaling of the wave functions to the system size, to identify whether a state is localized or delocalized. We find the disorder threshold for the existence of delocalized states in NC solids with different superlattice symmetries. To compare with the experimental *status quo*, in section 3.3 we use an effective-mass model to calculate the coupling strength, which is then compared with the coherent transport criterion. We find that NC solids treated with short organic ligands commonly used in photovoltaic devices are, in the optimum condition, on the margin of supporting delocalized states. In section 3.4, we develop a phenomenological model that includes the effect of the valley degeneracy present in lead-salt NCs. We show that the valley degeneracy have minor changes to the localization. We extend the model further to atomically coherent superlattice in section 3.5, where more detailed atomistic calculation results are readily available and can be used to parameterize our model. We show that these superlattice structure also has the potential to support delocalized trans-

port, albeit with a larger and therefore unfavorable size. In section 3.6, we discuss the relationship between fractal dimension and localization length. Major results presented in the chapter on have been published in Ref [27].

3.2 Calculation of Wave Function Delocalization

3.2.1 Tight Binding Model

We use the tight binding Hamiltonian to model NC solids.[20] The total Hamiltonian is

$$\begin{aligned} H &= H_{\text{onsite}} + H_{\text{coupling}} \\ &= \sum_i E_i a_i^\dagger a_i + \sum_{\langle i,j \rangle} t_{ij} (a_i^\dagger a_j + h.c.) \end{aligned} \quad (3.1)$$

Here E_i is the electronic state (HOMO or LUMO) of the NC at lattice point i . The sum over $\langle i, j \rangle$ includes all the nearest-neighbor pairs. t_{ij} is the coupling energy, which depends critically on the edge-to-edge distance between neighboring NCs,

$$t_{ij} = t_0 e^{-\kappa \Delta d_{ij}} \quad (3.2)$$

where t_0 is the coupling strength at average distance and Δd_{ij} is the deviation of the distance from the average distance. The exponential decay of coupling strength has been verified previously,[2, 28] and will be discussed further in the next section. As a first approximation, the dependence of coupling strength on NC diameter is neglected.

We use Monte Carlo simulation to model an ensemble of lattices, and calculate the density of states as well as the wave functions. The on-site energy disorder

s describes the inhomogeneous broadening of energy levels of the NCs, which is modeled as

$$P(E_i = E) \propto e^{-E^2/(2s^2)} \quad (3.3)$$

The positional disorder g describes the fluctuation of the position of each NC relative to a perfect superlattice, which is modeled as

$$P(\Delta x_i = \Delta x) \propto e^{-\Delta x^2/(2g^2)} \quad (3.4)$$

and $\Delta d_{ij} = \Delta x_j^{(\alpha)} - \Delta x_i^{(\alpha)}$, where α is the direction from lattice point i to lattice point j .

For NCs on the edge, both periodic boundary condition and hard boundary condition are implemented and show identical results. The size of the simulation is also verified to be large enough to converge to a fixed value. The complete Hamiltonian is then diagonalized. The eigenvalues corresponds to the energy of the states, and eigenvectors the corresponding wave functions. The analysis mostly follows previous approach.[20] To simplify the units, all energies will be given in terms of the dimensionless quantity E/t_0 , and all distances will be given in terms of the dimensionless quantity κx .

3.2.2 Inverse Participation Ratio and Fractal Dimension

We first consider the simple-cubic lattice. Each NC has six nearest neighbors. The calculated density of states (DOS) for $s/t_0 = 2.0$, $\kappa g = 0.2$ is plotted in Figure 3.1a. The calculation predicts formation of a symmetric mini-band with bandwidth around $12t_0$, centered at $E = 0$ (the average energy of uncoupled NC electron states), consistent with expectation. The DOS outside the mini-band

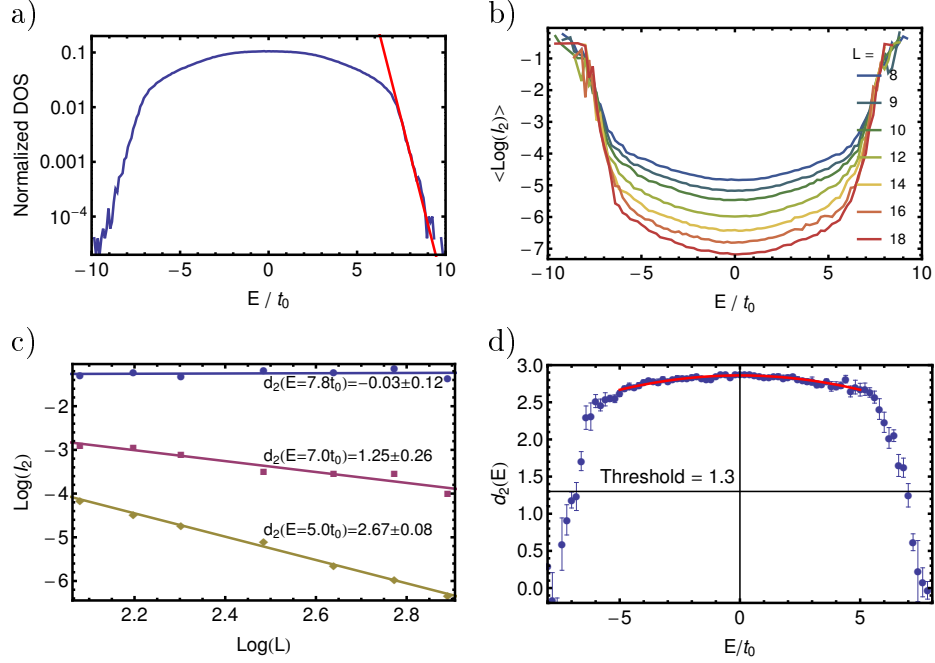


Figure 3.1: Simulation results for a 3D simple-cubic lattice. Parameters: $s/t_0 = 2.0$, $\kappa g = 0.2$. (a) Density of states. Red line is an exponential fit to the tail states. (b) Logarithm of I_2 (Inverse Participation Ratio) versus energy, different lines correspond to different system size L . (c) Scaling of I_2 versus the system size L . Solid lines are power-law fits. The opposite of the fitted exponent corresponds to d_2 , which is the fractal dimension. (d) Summary of the fractal dimension for all energies. Error bars are estimated from the fitting procedure. The red line is a parabolic fit of d_2 near the mini-band extremum.

shows an exponential decay, which is common among amorphous materials.[29, 30, 31, 32]

Since we are more interested in the wave functions, we use the inverse participation ratio[33]

$$I_2[\Psi_n] = \sum_r |\Psi_n(r)|^4 \quad (3.5)$$

to describe the degree of delocalization. Suppose the system is of size L and dimension d . If the wave function $\Psi_n(r)$ is completely delocalized, and in order to satisfy the wave function normalization ($\sum_r |\Psi_n(r)|^2 = 1$), $|\Psi_n(r)|$ has to be on the order of $L^{-d/2}$ for all lattice sites. This implies that $I_2[\Psi_n] \sim L^d (L^{-d/2})^4 \propto L^{-d}$.

On the other hand, if the wave function is completely localized, then $|\Psi_n(r)| \sim 1$ in the localized region, and $|\Psi_n(r)| \sim 0$ in other regions. This gives $I_2[\Psi_n] \sim \text{constant} \propto L^0$. At the transition from being delocalized to localized, the wave function is multifractal,[34] which gives $I_2[\Psi_n] \propto L^{-d_2}$, with d_2 the fractal dimension ($0 < d_2 < d$).

Figure 3.1b shows the average value of I_2 as a function of energy, for varying system size L . At fixed energy, we can fit I_2 to a power law function of L (Figure 3.1c), and extract $d_2(E)$ as the exponent. Here $E = 5.0t_0$ corresponds to states within the mini-band. As expected, $d_2(E) = 2.67$, which is close to 3 and so indicates that states are mostly delocalized. $E = 7.8t_0$ corresponds to states deep in the exponential band tail. Here $d_2(E) = 0$ within the uncertainty, which indicates that states at this energy are completely localized. At $E = 7.0t_0$, $d_2(E) = 1.24$, close to the critical point of transition, and the DOS has a fractal shape. $d_2(E)$ is plotted in Figure 3.1d.

It was shown previously that at the localization–delocalization transition, the scaling exponent $d_2 = 1.33 \pm 0.02$. [34] The scaling exponent is a universal quantity; it does not depend on the details of the coupling, but only on the dimension and symmetry of the interaction. If we draw a line at $d_2(E) = 1.33$, then statistically states below this line are delocalized, whereas states above it are localized (Figure 3.1d). Here, the transition points are at $E = \pm 6.8t_0$, which also correspond to the mobility edges.

There are two mobility edges, one on each side of the mini-band (if the band does not overlap with bands formed from higher-energy states). States that are within the mini-band are delocalized; states outside are localized. One can change the transport regime by moving the Fermi level of the electrons, by electrostatic

doping (via the gate voltage in a field effect transistor), or by electrochemical doping (changing the concentration of dopants).[35, 36] However, if the disorder is large enough, even the states at band center $E = 0$ are completely localized. In this case, all the states will be localized, and there is no coherent transport in the system.

Figure 3.2a summarizes the fractal dimension at band center ($d_2(E = 0)$) with varying on-site energy disorder s/t_0 and positional disorder κg for the simple cubic lattice. The black line ($d_2 = 1.33$) is the boundary between delocalized and localized states. For systems in the left bottom corner, there are some states that are delocalized, permitting the possibility of coherent transport; for systems on the top right corner, all the states are localized. The threshold with only on-site energy disorder and no positional disorder ($\kappa g = 0$, $s_{th}/t_0 = 6$) is consistent with previous results.[18]

Results for the body-centered cubic (bcc) lattice, face-centered cubic (fcc) lattice, and random close packing (rcp) are calculated in the same way and summarized in Figures 3.2b, c, d. The random close-packed assembly is generated with force-biased algorithms developed elsewhere.[37] The packing ratio generated is 64%, close to the theoretical limit of maximum packing.[38] (See Appendix 3.8.1 for detailed packing statistics.) Results for the 2D honeycomb, square and hexagonal lattices are also shown for comparison. Strictly speaking, all 2D systems with time-reversal symmetry have localized wave functions.[20] However, with low disorder, the localization length can be very long, much longer than the sample size, and therefore the states are only weakly localized. Here we use finite sample dimension L in the range of 10 to 40. Also, since there is no true Anderson transition here, we use $d_2 = 1.0$ as an approximate criterion. The actual value will be

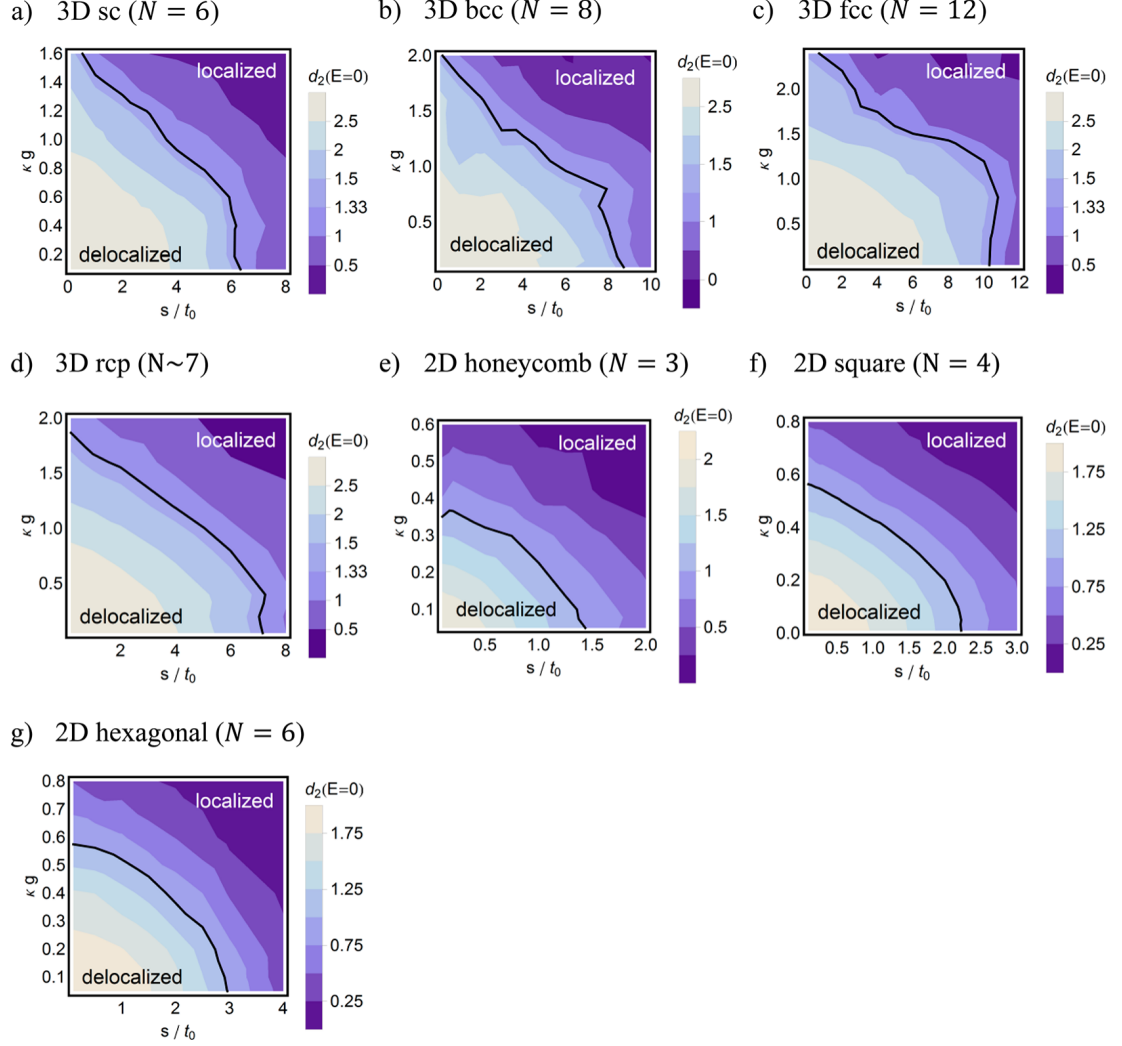


Figure 3.2: Contour plots for the fractal dimension $d_2(E)$ at band extremum, *versus* on-site energy disorder s/t_0 and positional disorder κg , for different crystal structures: (a) simple cubic (sc), (b) body-centered cubic (bcc), (c) face-centered cubic (fcc), (d) random close packing (rcp), (e) 2D honeycomb, (f) 2D square, and (g) 2D hexagonal. N is the number of nearest neighbors. $N \approx 7$ for random close packing is estimated from the cumulative pair distribution function.

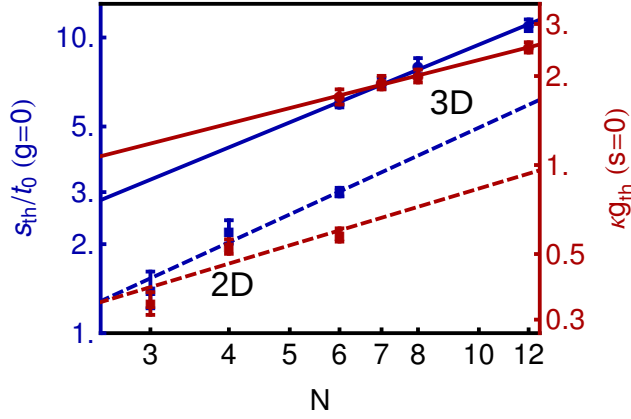


Figure 3.3: Threshold values for on-site energy disorder at $g = 0$ and positional disorder at $s = 0$. N is the number of the nearest neighbors. Solid lines are for 3D cases; dashed lines are for 2D cases; blue lines correspond to threshold for on-site energy disorder; red lines for positional disorder.

between 1.0 and 2.0.

3.2.3 Discussion

The basic shapes of all the phase diagrams are very similar. To analyze further, we plot the number of nearest neighbors *versus* critical on-site energy disorder s_{th} and critical positional disorder g_{th} in Figure 3.3.

The results for 3D lattices lie on a straight line, which indicates a power law dependence of critical disorder on the number of nearest neighbors. Fitting the result with $s_{th}/t_0 = A N^\alpha$ gives us the exponent $\alpha = 0.87 \pm 0.08$, which is close to 1. This can be understood as more neighbors introduce, on average, more coupling to each NC. The RMS bandwidth $\sqrt{\langle (E - E_0)^2 \rangle}$ for a perfect lattice without disorder is $N t_0$. This can be viewed as the total coupling energy of a single NC, considering all its nearest neighbors. The fitting of threshold positional disorder $\kappa g_{th} = B N^\beta$ yields the exponent $\beta = 0.54 \pm 0.09$, close to 0.5. This reflects the

model assumption that the positional disorder of each NC is independent. Thus, having more neighbors decreases the overall fluctuation of coupling energy of each NC, due to the central limit theorem.

It is worth mentioning that the point for 3D random close packing also fit well on the same power law curve. This implies that the lack of long range order does not affect the delocalization. This is very important, as most of the self-assembled NC arrays has amorphous structure. Indeed, extended states have been reported in disordered InGaAs/GaAs 2D quantum dot superlattices.[39] The explanation for this is that the allowed critical disorder s_{th}/t_0 for 3D crystalline superlattices are all much larger than 1, which means the allowed disorder is large enough that the coupling between adjacent NCs frequently approaches zero. This is effectively the same as a variable number of neighbors, as in the case of amorphous structure. On the other hand however, the disorder thresholds for 2D lattices are all significantly lower than those of 3D lattices, even after considering their smaller number of nearest neighbors. This indicates that dimensionality does play an important role in localization.

3.3 Effective Mass Calculation of Coupling Energy

It is clear that the existence of coherent transport depends critically on the ratio of the on-site energy disorder to the coupling strength. There have been numerous attempts to estimate the coupling strength in experiments. A large red shift in the peak position of the absorption spectrum is usually seen when quantum dots are deposited on a solid film with short ligands, and the red shift is frequently attributed to the electronic coupling.[2, 40] However, further experiments[41] showed

that other factors, such as polarization effects, are more likely to be the cause. Application of the results above will require estimates of the coupling energy, and calculations will shed light on the relationship between coupling energy and optical spectra.

3.3.1 1-band Effective Mass Model for Nanocrystal Assemblies

We use a single-band effective mass model to analyze the magnitude and distance dependence of inter-NC coupling. The single-band model is only a rough approximation to the actual band structure. However, it is mathematically simple to evaluate, it gives a clear physical picture, and the energy levels it produces agree reasonably well with more-sophisticated models and experiments, especially for large particles.[42] We believe that the model is effective because the coupling energy depends more on the barrier height at the NC-host interface than on the electronic structure of the NC or host material.

The Schrödinger Equation for the one-band model is [43]

$$-\nabla \left(\frac{\hbar^2}{2m_{eff}(\mathbf{r})} \nabla \right) \phi(\mathbf{r}) + V(\mathbf{r}) \phi(\mathbf{r}) = E_0 \phi(\mathbf{r}) \quad (3.6)$$

$$\text{where } [m_{eff}(\mathbf{r}), V(\mathbf{r})] = [m_{eff}(r), V(r)] = \begin{cases} [m_{NC}, -V_{well}], & r \leq R \\ [m_{env}, 0], & r > R \end{cases} \quad . \quad m_{NC}$$

is the effective mass of the electron (or hole) for the bulk semiconductor of the nanocrystal; m_{env} is the effective mass of the electron (or hole) of the interstitial area; and V_{well} is the potential-energy barrier. The lowest energy wave function

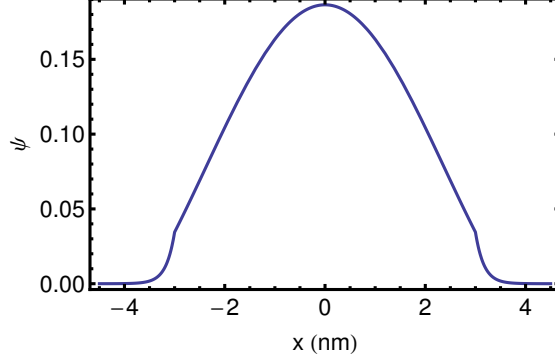


Figure 3.4: Wave function of electron in a nanocrystal, calculated from a single-band effective mass model. Parameters used: $m_{NC} = m_{PbS} = 0.09 m_e$ (m_e is the free electron mass), $m_{env} = m_C = 0.28 m_e$, $V_{well} = 4.6$ eV, $R = 3$ nm.

has the form:

$$\phi(\mathbf{r}) = \phi(r) = \begin{cases} \frac{C_1 \sin kr}{r}, & r \leq R \\ \frac{C_2 e^{-\alpha r}}{r}, & r > R \end{cases} \quad (3.7)$$

where $k = \sqrt{2m_{NC}(E + V_{well})/\hbar^2}$, $\alpha = \sqrt{2m_{env}(-E)/\hbar^2}$. The wave function (Shown in Figure 3.4) is continuous at the boundary, but has a discontinuous derivative due to the discontinuity of effective mass across the boundary.

The Hamiltonian for a superlattice of coupled NCs is

$$\begin{aligned} H(\mathbf{r}) &= -\nabla \left(\frac{\hbar^2}{2m_{eff}(\mathbf{r})} \nabla \right) + V(\mathbf{r}) \\ &= -\nabla \left(\frac{\hbar^2}{2m_{env}} \nabla \right) + \sum_n \eta(|\mathbf{r} - \mathbf{R}_n| < R) \left[-\nabla \left(\left(\frac{\hbar^2}{2m_{NC}} - \frac{\hbar^2}{2m_{env}} \right) \nabla \right) - V_{well} \right] \\ &= -\nabla \left(\frac{\hbar^2}{2m_{env}} \nabla \right) + \sum_n H'(\mathbf{r} - \mathbf{R}_n) \end{aligned} \quad (3.8)$$

We assume that the total wave function is a linear combination of the “atomic” wave functions centered on the NCs:

$$\psi(\mathbf{r}) = \sum_n a_n \phi(\mathbf{r} - \mathbf{R}_n) \quad (3.9)$$

Inserting Eq. 3.9 into Eq. 3.8 and taking the inner product with the wave function

yields

$$a_m \sum_{n \in \mathcal{N}_m} f_2(d_{mn}) + \sum_{n \in \mathcal{N}_m} a_n f_3(d_{mn}) = (E - E_0) \left(a_m + \sum_{n \in \mathcal{N}_m} a_n f_1(d_{mn}) \right) \quad (3.10)$$

$\mathcal{N}_m$ is the set containing all the nearest neighbors of the NC at lattice site m . Here only the lowest-order overlap integrals between nearest neighbors are kept, and

$$\begin{aligned} f_1(d_{mn}) &= \int d^3r \phi^*(\mathbf{r} - \mathbf{R}_m) \phi(\mathbf{r} - \mathbf{R}_n) \\ f_2(d_{mn}) &= \int d^3r \phi^*(\mathbf{r} - \mathbf{R}_m) H'(\mathbf{r} - \mathbf{R}_n) \phi(\mathbf{r} - \mathbf{R}_n) = I_{mnm} \\ f_3(d_{mn}) &= \int d^3r \phi^*(\mathbf{r} - \mathbf{R}_m) H'(\mathbf{r} - \mathbf{R}_m) \phi(\mathbf{r} - \mathbf{R}_n) = I_{mmn} \end{aligned} \quad (3.11)$$

The integrals in Eq. 3.11 can be evaluated as

$$\begin{aligned} I_{ijk} &\equiv \int d^3r \phi^*(\mathbf{r} - \mathbf{R}_i) H'(\mathbf{r} - \mathbf{R}_j) \phi(\mathbf{r} - \mathbf{R}_k) \\ &= \int_{|\mathbf{r} - \mathbf{R}_j| < R} d^3r \left(\frac{\hbar^2}{2m_{NC}} - \frac{\hbar^2}{2m_{eff}} \right) \nabla \phi^*(\mathbf{r} - \mathbf{R}_i) \nabla \phi(\mathbf{r} - \mathbf{R}_k) \\ &\quad - V_{well} \phi^*(\mathbf{r} - \mathbf{R}_i) \phi(\mathbf{r} - \mathbf{R}_k) \end{aligned} \quad (3.12)$$

Since $f_1 \ll 1$, it can be neglected on the right side of Eq. 3.10, and this leaves

$$\left(E_0 + \sum_{n \in \mathcal{N}_m} f_2(d_{mn}) \right) a_m + \sum_{n \in \mathcal{N}_m} f_3(d_{mn}) a_n = E a_m \quad (3.13)$$

Eq. 3.13 can be interpreted physically as this: the f_2 diagonal term shifts the energy level of uncoupled NCs due to the wave function leaking into neighboring NCs. Positive f_2 blue-shifts the peak, and negative f_2 red-shifts the peak. The integral I_{mnm} for f_2 has two parts: the kinetic-energy part and the potential-energy part. The kinetic energy part is positive, because $m_{NC} < m_{env}$ (for most semiconductors), whereas the potential energy part is negative, because $-V_{well} < 0$. This contrasts with tight-binding models for ordinary solids, where the free-electron mass is used everywhere. Therefore, it is not immediately apparent whether f_2 is positive or negative, or whether it will shift the energy up or down. The f_3 off-diagonal term

introduces coupling between adjacent NCs, and leads to possible band formation. On the other hand, it does not change the trace of the Hamiltonian, and therefore does not change the average energy.

3.3.2 Numerical Results

The effective masses of electrons in the nanocrystal are obtained from the literature and listed in the Appendix 3.8.2. For the organic alkane chain, a previous study[44] used density functional theory and pseudopotentials to calculate the complex band-structure of linear alkane chains. It predicts an exponential decay $e^{-\beta d}$ ($\beta \sim 0.8 \text{ \AA}^{-1}$) of both electron and hole transport through the chain, and agrees very well with a number of experimental measurements[2, 28] of carrier mobility in NC solids.

In the effective-mass model and WKB approximation, $\beta = 2\kappa \approx 2\sqrt{2m_{env}V_{well}/\hbar^2}$. Thus, one would expect that the coupled wave function depends critically on the product $m_{env} V_{well}$ but barely on the individual value of m_{env} or V_{well} (as verified in the Appendix 3.8.3). The numerical values of the overlap integrals are plotted in Figure 3.5a, for $V_{well} = 4.0 \text{ eV}$, $m_{env} = m_{eff,C} = 0.162m_0$, $m_{NC} = m_{PbSe} = 0.047m_0$, and $R = 3 \text{ nm}$. The kinetic term and static potential term are plotted individually. We see that $|f_{2k}| > |f_{2p}|$, and therefore the total $f_2 = f_{2k} + f_{2p}$ is small but positive. f_{3k} and f_{3p} have the same sign (their absolute phase depends on the phase of the wave across different NCs, but their relative phase is determined). Fits of the absolute values of the overlap integrals to exponential decays are shown in Figure 3.5b. It is clear that f_3 follows an exponential decay $Ae^{-\kappa d}$ (with $\kappa = 0.40 \text{ \AA}^{-1} \approx \beta/2$), whereas f_2 follows approximately an $e^{-2\kappa d}$ decay.

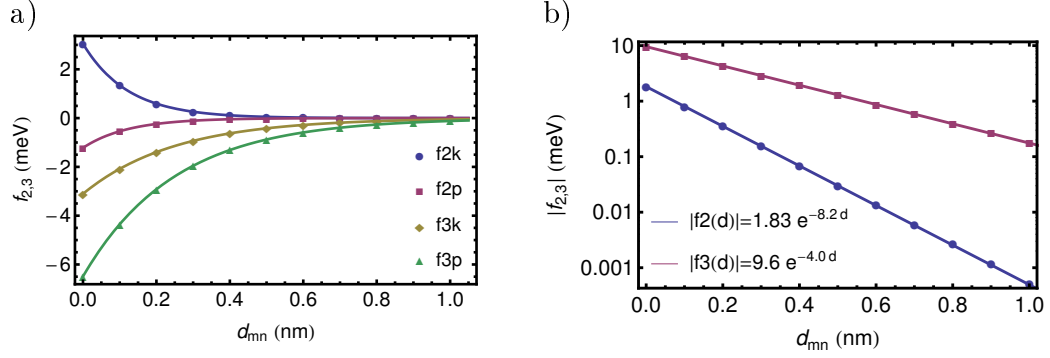


Figure 3.5: (a) Values of the overlap integrals as a function of edge-to-edge distance between NCs. Integral due to kinetic energy and potential energy are plotted individually. $V_{well} = 4.0 \text{ eV}$, $m_{env} = m_{eff,C} = 0.162 m_0$, $m_{NC} = m_{PbSe} = 0.047 m_0$, $d = 6 \text{ nm}$. (b) Exponential fit of the overlap integrals.

To study the size dependence of coupling and disorder, we use ethanedithiol (EDT), a short linker molecule commonly used in NC devices. The molecule length is about 0.4 nm . [2, 28] The coupling energy t_0 for NCs connected by EDT is plotted as a function of diameter for different materials in Figure 3.6a. The on-site energy disorder s is estimated using a four-band model for lead salt NCs, [42] and a one-band model for cadmium salt NCs. For CdS and CdSe, only electron transport is considered, and it is generally found that the electron mobility is higher than the hole mobility. [45, 10, 46] The NC diameter is assumed to vary with a standard deviation of 0.3 nm , [2, 47] which corresponds to one layer of crystal lattice. The ratio of disorder to coupling is plotted in Figure 3.6b. Smaller NCs are more favorable for delocalized transport, due to their larger coupling strength. For fixed size, PbSe NCs are the most favorable for delocalization, and CdS the least favorable.

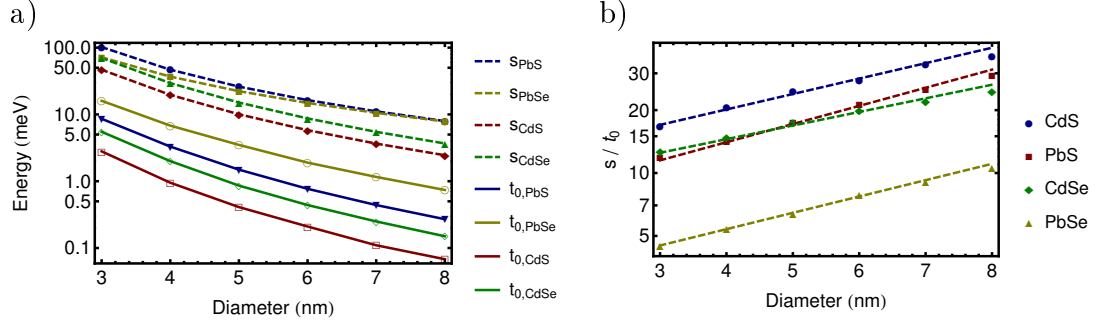


Figure 3.6: Summary of calculated coupling energy t_0 for EDT coupled nanocrystals, and on-site energy disorder s . (a) shows the absolute values. s is calculated assuming standard deviation in NC diameters is 0.3 nm for all sizes; t_0 is calculated assuming surface to surface distance between NCs is 0.4 nm. (b) shows the relative ratio of s and t_0 .

3.3.3 Discussion

The electronic coupling itself does not lead to a red shift in absorption. We saw previously that f_2 is a diagonal term, which only shifts the overall energy and does not contribute to the actual delocalization of the wave function, and *vice versa* for f_3 . We also saw that f_2 is always orders of magnitude smaller than f_3 in absolute value. Furthermore, f_2 is actually slightly positive. When the wave function of one NC leaks into an adjacent NC, the kinetic energy it picks up is larger in magnitude than the decrease in potential energy, so the overall energy increases slightly. As a result, if only electronic coupling is considered, the absorption peak position should shift to shorter rather than longer wavelengths. Therefore, the observed red-shift must arise from other processes. We would like to point out, however, that electronic coupling does red-shift the absorption edge (as opposed to the peak) because of the much larger f_3 . Broadening of the absorption peak is a direct measure of electronic coupling.

One explanation for the observed red-shift is the sulfur atom in the thiol group. The majority of experiments on ligand exchange uses thiol group to bond the ligand

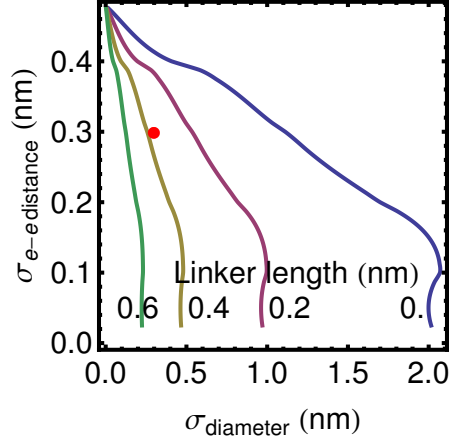


Figure 3.7: Summary of critical disorder for diameter fluctuation $\sigma_{diameter}$ and edge-to-edge distance fluctuation $\sigma_{e-e\ distance}$ for 3 nm PbSe NCs, for average edge-to-edge distances of 0, 0.2, 0.4, and 0.6 nm. The red dot is for EDT-coupled dots. It lies in the proximity of the yellow line (0.4), indicating marginal delocalization.

onto NC surface due to thiol's strong affinity to the NC surface. The sulfur atom in thiol group can partially integrate into the original lattice, making the NC slightly bigger, thus causing the red shift. Another explanation is the increase of the dielectric constant when the NCs are closer. The effect of dielectric contrast between the NC and host medium is not included in the calculation. In most cases, the dielectric constant of the NC is much larger than that of the medium. For example, $\epsilon_0(\text{PbS}) = 17$, $\epsilon_0(\text{PbSe}) = 23$, while $\epsilon_0(\text{air}) = 1$, $\epsilon_0(\text{polyethylene}) = 2.25$. In that case, the image charge at the interface has the same sign as the original charge, which repels the charge from the interface, causing “dielectric confinement”. A more densely packed NC film will have a higher effective dielectric constant for the surrounding medium, which reduces the dielectric confinement, also causing red shift.

Figure 3.7 shows the critical values of the disorder for 3 nm diameter PbSe quantum dots with different linker lengths, plotted in units of the measurable quantities. For an EDT-coupled NC solid with diameter fluctuations of 0.3 nm

and edge-to-edge distance fluctuations of 0.3 nm, the point lies close to the delocalization threshold.

To achieve coherent transport, the system has to be well within the delocalization threshold to have a considerable energy band. As seen from Figure 3.7, if the edge-to-edge distance is less than 0.4 nm, it will be on the threshold of having delocalized states. NC solids passivated with metal chalcogenide complex[10] and atomic ligands[4] both show much improved carrier mobility. To decrease the positional disorder κg , much progress has been made to improve g in terms of superlattice formation. Recently, atomically coherent PbSe superlattices have been reported.[48, 49, 50] Due to the constraints of the superlattice structures, their positional disorder will be significantly improved. We'll discuss these structures in more details in the later sections. However, another way to decrease positional disorder is to decrease κ , by infilling the void space of the solid with a small-bandgap semiconductor. The use of atomic layer deposition[4] proves to be an excellent way to passivate the nanocrystal surface while decreasing the energy barrier between nanocrystals.

3.4 Effects of Valley Degeneracy in Lead-Salt Nanocrystals

One aspect that is missing from the previous analysis is the 8-fold degeneracy in the HOMO and LUMO levels of PbS or PbSe NCs, due to the four equivalent L valleys in the bulk band structure, and the 2-fold spin degeneracy. Coupling between the valleys due to quantum confinement then splits this degeneracy. The exact nature of the coupling and the resulting splitting of the energy levels are currently unknown. As far as we know, there are no experiments that directly measure this

valley coupling strength, although there are numerous observations of the splitting or broadening of lowest exciton states that suggest its existence.[51, 52, 53, 54] Nevertheless, first principle calculations estimate the splitting due to inter-valley coupling to be $10 - 80$ meV, for PbSe dots ranging from $3 - 8$ nm, which shows oscillatory behavior and is sensitive to size.[55, 56] This energy is on the same order of magnitude as the coupling energy between adjacent dots and the on-site energy disorder, and therefore suggests that it could appreciably affect the delocalization of electron states. The simplest intuition might be that splitting of energy levels comparable to the coupling energy should lead to enhanced coupling and transport. We use a phenomenological model to study 4-nm-diameter PbSe NC simple-square-lattice and simple-cubic-lattice as examples to evaluate the impact of inter-valley coupling on delocalization.

3.4.1 Phenomenological Inter-valley Coupling Model

To describe the degeneracy and coupling for four valleys, each state in the original single-valley model is expanded into four states, with inter-valley coupling V_{int} between them:

$$E_0 \rightarrow \begin{pmatrix} E_0 & V_{int}e^{i\phi} & V_{int}e^{i\phi} & V_{int}e^{i\phi} \\ V_{int}e^{-i\phi} & E_0 & V_{int}e^{i\phi} & V_{int}e^{i\phi} \\ V_{int}e^{-i\phi} & V_{int}e^{-i\phi} & E_0 & V_{int}e^{i\phi} \\ V_{int}e^{-i\phi} & V_{int}e^{-i\phi} & V_{int}e^{-i\phi} & E_0 \end{pmatrix} \quad (3.14)$$

Here ϕ is the phase of the coupling. Depending on the exact value of ϕ , the splitting of the energy levels will be different. Nevertheless, the total energy splitting is consistently 4 times V_{int} . (See Appendix 3.8.4 for details.) From the total energy splitting previously reported,[55, 56] we estimate $V_{int} \cong 15$ meV for 4 nm PbSe

NCs.

Each coupling term between adjacent NCs in a single-valley model is also expanded into a 4×4 matrix that describes coupling across different valleys:

$$t \rightarrow t * \begin{pmatrix} \alpha & \beta & \beta & \beta \\ \beta & \alpha & \beta & \beta \\ \beta & \beta & \alpha & \beta \\ \beta & \beta & \beta & \alpha \end{pmatrix} \quad (3.15)$$

where t is the coupling strength in the single-valley model, which has an exponential dependence on the distance between dot surfaces, α is the parameter that describes the valley selectivity of the coupling, $\alpha^2 + 3\beta^2 = 1$ so as to preserve the total tunneling probability from one valley in a dot to the adjacent dot. $\alpha = 1$ ($\beta = 0$) corresponds to the case where an electron in one valley is only coupled to the electron state in the adjacent dot in the same valley; $\alpha = 0.5$ ($\beta = 0.5$) corresponds to the case where an electron in one valley is equally coupled to all four valleys in the adjacent dot.

3.4.2 Wave Function Delocalization in Multi-valley Model

First we consider the simple case where $\alpha = 1$. Figure 3.8 compares the fractal dimensions of the original single-valley model and the multi-valley model with different V_{int} . In the case of $V_{int} = 0$, and since $\beta = 0$, all four valleys in the NC solid are completely decoupled. As expected, the fractal dimension stays the same. When V_{int} is increased, the maximum fractal dimension stays the same, while the overall bandwidth is increased. We also tested different scenarios for disorder (predominately on-site energy disorder, predominately positional disorder, etc.) The trend is consistent across all cases. (See Appendix 3.8.5 for more details)

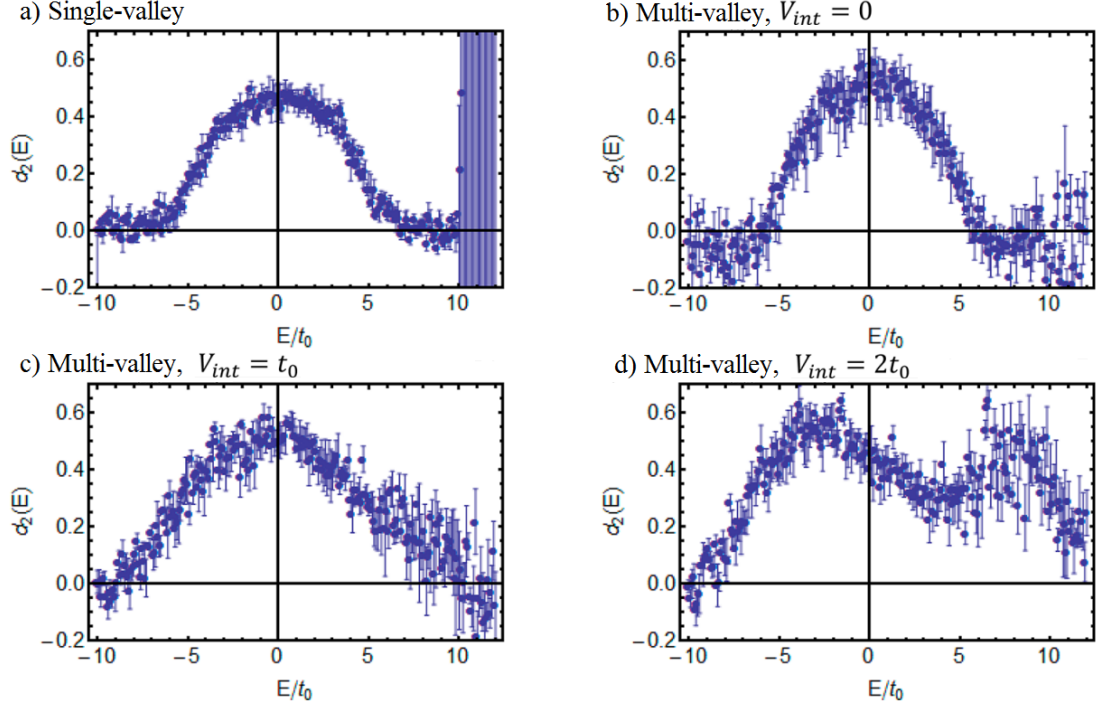


Figure 3.8: Fractal dimension $d_2(E)$ for different valley coupling model. (Noise in the data is due to limited calculation times and has no physical meaning.) Parameters: $s/t_0 = 1.5$, $\kappa g = 0.6$, $\phi = 0$.

Next, we consider the effect of coupling selectivity. Figure 3.9 shows the fractal dimension for different α values. Most noticeable is when $\alpha = 0.5$, where a “localization band” appears from $E = -5t_0$ to $E = 0$: the states are almost completely localized. This is caused by the destructive interference of coupling to the next NC from different valleys: the coupling matrix has an eigenvalue of 0 at $\alpha = 0.5$; the corresponding eigenstate represents a state which has no coupling to its adjacent NCs and is therefore completely localized. Away from the localization band, the system shows improved delocalization compared with the one-band model.

Intermediate values of α produce the best potential for transport. Appendix 3.8.5 summarizes the results for different disorders for $\alpha = 0.8$. The increase of delocalization is largest when the on-site energy disorder is large. Compared with the one-band model, the increase of maximum is equivalent to the reduction

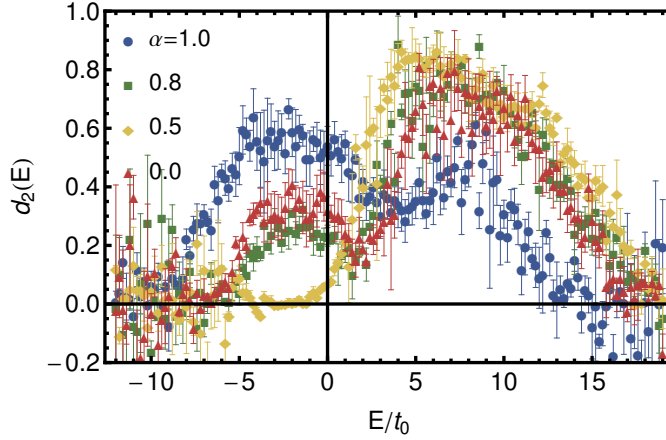


Figure 3.9: Fractal dimension $d_2(E)$ for different coupling selectivity α . Parameters: $s/t_0 = 1.5$, $\kappa g = 0.6$, $\phi = 0$, $V_{int} = 2.0 t_0$.

of on-site energy disorder by $0.9 - 1.4 t_0$. Calculations for 3D lattices are also listed in the Appendix 3.8.6, and show similar results. The inter-valley coupling increases the bandwidth of delocalization by approximately $4V_{int}$. The localization band is also present and is even more prominent than in the 2D case. The net result is that in some cases, the maximum delocalization is slightly decreased instead of increased. We estimate that the increase in wave function delocalization due to inter-valley coupling corresponds to the increase that would result from a reduction of on-site energy disorder by about t_0 .

3.4.3 Discussion

There is currently no way to identify which model is more accurate than the other. What we conclude from the analysis is that inter-valley coupling does change the delocalization spectrum appreciably. For $\alpha = 1.0$, valley coupling increases the bandwidth; for $\alpha = 0.5$, it creates a localization band; for intermediate α , it effectively decreases on-site energy disorder by about t_0 . We expect that first-principle calculations will provide new data that can help identify the true value of

α . Also, low-temperature charge transport experiments over a large doping range might provide experimental evidence for the localization band. On the other hand, the ratio of on-site energy disorder to coupling energy is generally very large ($\gtrsim 8$) for current synthesis capabilities, and a change of 1 is not going to significantly impact the delocalization.

3.5 Disorder in Atomically Coherent Nanocrystal Superlattices

There is one case where detailed coupling between NCs has been more carefully studied. Recently, a new type of NC superlattices was made, called atomically coherent nanocrystal superlattices (ACNS). (TEM image, statistics) In these superlattices, the NCs have facets that are fused together. The crystal planes of each NC are perfectly aligned, creating a single crystalline domain that can extend up to several microns.[48, 50, 49] In these structures, the coupling strength between NCs increases, due to lack of organic or inorganic spacers in between. The structural disorder is also significantly reduced, owing to the superlattice constraint. Also, when their facets fuse together, the coupling energy between neighboring NCs scales approximately as a linear function of the number of atoms at the neck region,[57, 58] instead of an exponential function of their surface to surface distance. Only the on-site energy disorder is expected to be slightly worse, due to the extra disorder introduced during the necking process. All in all, it is expected that electron transport in ACNS will be significantly improved, compared with ordinary NC assemblies.

The electronic states of ACNS were studied using atomistic tight-binding

calculations.[57, 58] In a perfect lattice, wave functions are periodic over one superlattice lattice constant (up to a certain phase). As a result, the calculation only needs to include all the atoms in one NC (on the order of 1000), making it computational feasible to calculate the band structure of the superlattice using *ab-initio* methods. However, it is difficult if not impossible to include disorder into the calculation as that will require at least hundreds of NCs, thus mounting to millions of atoms, in order to properly describe disorder in the structure.

On the other hand, a properly constructed tight-binding model, where each NC is treated as one atom, should describe the system well. Despite the fact that the coupling energy between neighboring dots is greatly increased (10s meV), it is still much smaller than the quantum confinement energy for each NCs (100s meV). In other words, coupling is still a small perturbation upon the original energy levels created by the quantum size effect. As a result, it is reasonable to assume that a tight-binding model, where each NC is treated as an entity, can very well describe the entire superlattice.

Here, we construct a parametric tight-binding model, with consideration of appropriate symmetry in NCs. We fit the model to the *ab-initio* calculated band-structure for simple square lattice, and obtain all the parameters in the model. Then we use this parametric model to evaluate the effect of disorder on the electronic states.

3.5.1 Fitting Band Structure with Inter-valley Coupling Model

We treat each NC as an atom with 4 states, which correspond to the electron states originated from the four L-valleys:

$$H_i = \begin{pmatrix} E_s & V_0 e^{i\phi} & V_0 e^{i\phi} & V_0 e^{i\phi} \\ V_0 e^{-i\phi} & E_s & V_0 e^{i\phi} & V_0 e^{i\phi} \\ V_0 e^{-i\phi} & V_0 e^{-i\phi} & E_s & V_0 e^{i\phi} \\ V_0 e^{-i\phi} & V_0 e^{-i\phi} & V_0 e^{-i\phi} & E_s \end{pmatrix} \quad (3.16)$$

Neighboring NCs are coupling through a tight-binding formula:

$$H = \begin{pmatrix} H_1 & H_{12} & \cdots & H_{1n} \\ H_{21} & H_2 & \cdots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \cdots & H_n \end{pmatrix} \quad (3.17)$$

where

$$H_{ij} = \begin{cases} \begin{pmatrix} V_{\alpha\alpha} & V_{\alpha\beta} & V_{\alpha\beta} & V_{\alpha\beta} \\ V_{\alpha\beta} & V_{\alpha\alpha} & V_{\alpha\beta} & V_{\alpha\beta} \\ V_{\alpha\beta} & V_{\alpha\beta} & V_{\alpha\alpha} & V_{\alpha\beta} \\ V_{\alpha\beta} & V_{\alpha\beta} & V_{\alpha\beta} & V_{\alpha\alpha} \end{pmatrix} & , \text{ if } i, j \text{ are adjacent} \\ 0 & , \text{ if } i, j \text{ are not adjacent} \end{cases} \quad (3.18)$$

$V_{\alpha\alpha}$ corresponds to the coupling between valleys in the same direction in neighboring NCs. $V_{\alpha\beta}$ corresponds to coupling between different valleys. It depends on the relative orientation of the valleys and the direction of the bond. In simple square or simple cubic lattice, there are two different orientation altogether, which

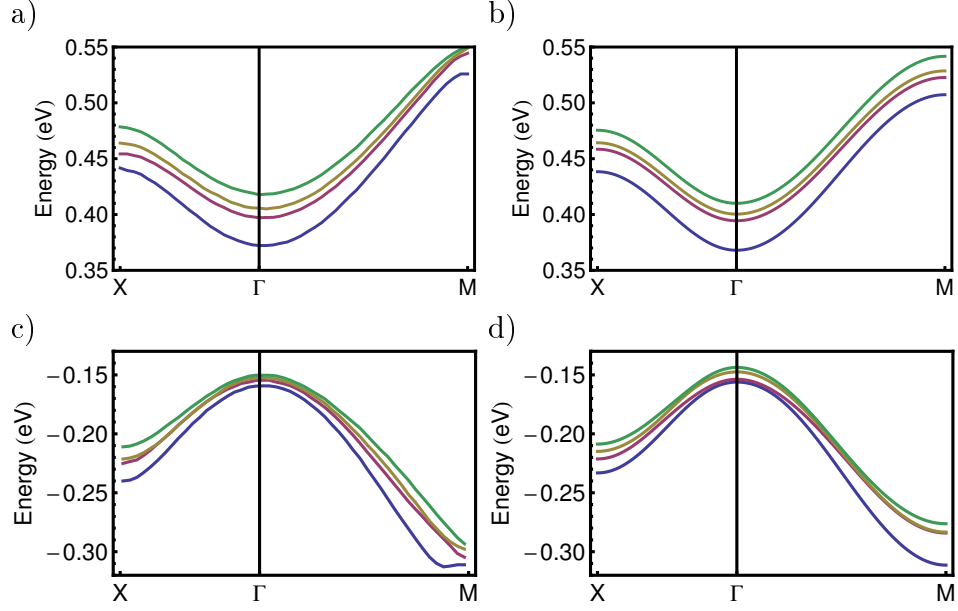


Figure 3.10: Lowest conduction band (a),(b) and highest valence band (c),(d) of a square lattice of 4.89 nm PbSe NCs. (a),(c) are reproduced from literature which used atomistic calculation. (b),(d) are calculated using the effective tight-binding Hamiltonian. Zero point in energy is the valence band maximum for bulk PbSe.

are assigned as $V_{\alpha\beta,0}$ and $V_{\alpha\beta,90}$. See Appendix 3.8.7 for details. The ansatz wave function is the Bloch wave function over the superlattice. The corresponding band structure is calculated based on the tight-binding Hamiltonian. A least square fitting against the *ab-initio* results [57] is then implemented on the six parameters in the model: E_s , V_0 , ϕ , $V_{\alpha\alpha}$, $V_{\alpha\beta,0}$ and $V_{\alpha\beta,90}$ to obtain optimal fitting.

The fitted lowest conduction band (CB) and highest valence band (VB) for 4.89 nm diameter PbSe NCs CBC is plotted in Figure 3.10 with parameters summarized in Table 3.1. Those correspond to NCs with $n = 8$ PbSe unit cells across, and truncation factor $q = 0.45$, i.e., the neck region is 45% wide compared with the diameter of the NC.

The six parameters each control different aspect of the bandstructure. E_s determines the average energy; $V_{\alpha\alpha}$ determines the overall band shape; V_0 determines

	E_s	V_0	ϕ	$V_{\alpha\alpha}$	$V_{\alpha\beta,0}$	$V_{\alpha\beta,90}$
CB (4.89 nm)	0.459	0.0078	2.00	-0.0165	-0.0006	-0.00056
VB (4.89 nm)	-0.220	0.0044	2.59	0.0173	0.0020	0.00029
CB (4.28 nm)	0.523	0.0060	1.96	0.0188	-0.0035	0.00004
VB (4.28 nm)	-0.265	0.0078	2.21	-0.0186	0.0032	-0.00024

Table 3.1: Parameters used in the fitting of square lattice for 4.89 nm diameter PbSe NCs and 4.28 nm PbSe NCs. Units: eV.

the average splitting of the four bands; the phase ϕ determines degeneracy splitting at Γ point; $V_{\alpha\beta,0}$ and $V_{\alpha\beta,90}$ together changes the relative degeneracy splitting at X point and M point. Directly estimating the error on each parameter is difficult, but we expect the least error with respect to E_s (± 0.005 eV) and $V_{\alpha\alpha}$ (± 0.0005 eV) and slightly larger errors with respect to the other four parameters.

Compared with *ab-initio* results[57], the effective Hamiltonian captures all the essential features of the band-structure. A few things can be extracted from the fitting parameters. First, the fitted inter-valley coupling strength in the same NC (V_0) is around 4 – 8 meV, consistent with other *ab-initio* calculations with individual NC.[55] Second, the coupling energy across NCs in the same valley ($V_{\alpha\alpha}$) is an order of magnitude larger than in different valleys ($V_{\alpha\beta,0}, V_{\alpha\beta,90}$). Third, the coupling energy between adjacent NCs ($V_{\alpha\alpha}$) is about 3 – 4 times larger than the coupling energy between NCs of similar sizes connected with EDT ligand, showing the benefit of fused surface.

In the atomistic calculation,[57] it was stressed that the sign of the coupling strength ($V_{\alpha\alpha}$) depends on whether the number of biplanes in the NCs constructed for the superlattices is even or odd,(also see Table 3.1) and that affects whether the conduction band minimum and valence band maximum is at Γ or M point. We believe that the difference is artificial, and does not carry physical consequences. The sign of the basis function of the tight-binding model is not fixed. In a square or

cubic superlattice, one can choose a particular set of basis so that the wave function of every other NCs switches sign, and thus the sign of the coupling strength $V_{\alpha\alpha}$ and $V_{\alpha\beta}$ reversed. Another way to look at this is to look in the extended Brillouin zone scheme. A shift in the phases of the base function is equivalent to moving the Brillouin zone center from Γ point to M point.

3.5.2 Delocalization of Wave function for ACNS

We then use this effective Hamiltonian to study the wave function localization with disorder. Two major disorders are present in this structure: the fluctuation of the size of each NC and the fluctuation of the “neck” width of the bond between NCs. The size fluctuation is modeled as a Gaussian fluctuation of the energy levels in each NC. For a first order approximation, all four states in the NC are shifted together, thus accounting for the size dependence of the quantum confinement effect but not the valley coupling effect. The “neck” width disorder causes fluctuation of the coupling strength between NCs, which is proportional to the number of atoms in the neck region.[57, 58]

The energy fluctuation is estimated from 4-band PbSe NC calculation[42] to be 23 meV for 0.3 nm diameter fluctuation for 4.89 nm diameter PbSe NCs. The bond width from the statistical analysis of TEM pictures is 7.5 ± 2.8 (unit: lattice constant). It was also estimated that 21% of bonds aren’t connected at all. Figure 3.11 shows the calculated fractal dimensions d_2 as a function of energy.

It is clear that the requirement for wave function delocalization is still stringent, and that in the current disorder, the wave function is still localized. Even if we have a perfectly aligned crystal, while keeping the same NC size dispersion, as in

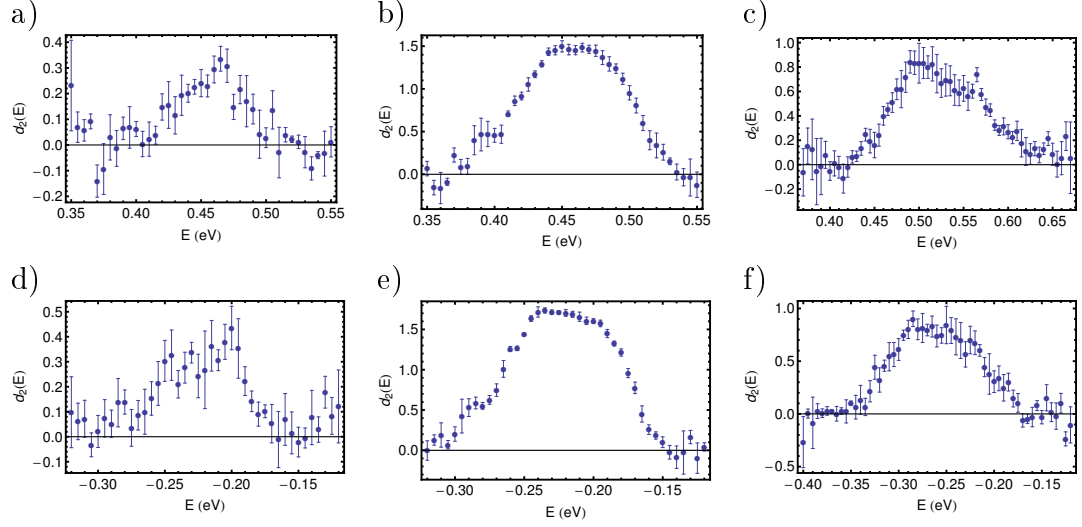


Figure 3.11: Calculated fractal dimension d_2 for conduction band (a),(b),(c) and valence band (d),(e),(f). Parameters: NCs diameter 4.89 nm. $s = 23$ meV is the energy fluctuation due to NC size dispersion. In (a) and (d), $P_0 = 21\%$ is the probability of a nonexistent bond between adjacent NCs. $N = 7.5 \pm 2.8$ (unit: lattice constant) is the projected number of atoms across the bond (in one direction). The bond strength is proportional to the number of atoms at the cross section, thus proportional to N^2 . In (b) and (e), $s = 23$ meV, $P_0 = 0$, $N = 7.5 \pm 0.0$. In (c) and (f), NCs size is decreased to 4.28 nm, $s = 32$ meV, $P_0 = 21\%$, $N = 7.5 \pm 2.8$.

Figure C2 (b),(e), the delocalization is only slightly improved. If we decrease the NC diameter, thus increase the coupling between adjacent NCs, while keeping the same amount of disorder, the delocalization is also slightly improved. These results indicate that complete delocalization of wave function across the whole superlattice is still difficult.

3.5.3 Discussion

This difficulty in transport results from a few factors. First, states in a 2D system is inherently more localized than in a 3D systems. As shown previously, the threshold disorder is at least twice as big in 3D systems as in 2D systems. Currently, making

highly ordered 3D cubic superlattice is still in progress. Second, the current method to assemble NCs into highly ordered structures requires relatively large NCs ($\gtrsim 5$ nm), which have more prominent facets. The ratio of coupling strength *vs.* onsite energy disorder is another factor of two larger for 3 nm NCs compared with 5 nm NCs. Thus, making 3D superlattice made of smaller NCs is the way to go into the delocalized transport regime.

3.6 Localization Length *vs.* Fractal Dimension

Fractal dimension is a good characterization of the overall degree of delocalization of the electron wave functions. However, it is somewhat abstract and sometimes difficult to directly connect with experiments. In the localized regime, coherent length or localization length is a quantity that is more intuitive and physically explicit. It is the size of a localized wave function. Since both fractal dimension and localization length are describing the same thing — the degree of localization, it is expected that there will be a one-to-one correspondence between them. We use a 2D square lattice of a single-band model to illustrate that this is indeed the case.

3.6.1 Transfer Matrix Formalism

This section is adapted from reference [19]. The Schrödinger's equation for 2D square lattice is

$$H |\Psi\rangle = \left(\sum_i H_i |i\rangle \langle i| + \sum_{\langle i,j \rangle} H_{ij} |i\rangle \langle j| \right) |\Psi\rangle = E |\Psi\rangle \quad (3.19)$$

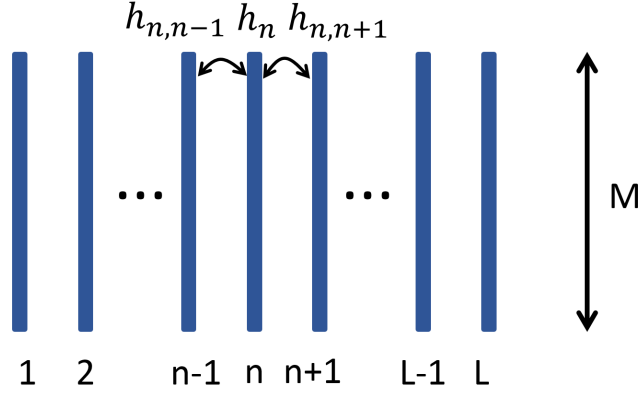


Figure 3.12: Schematic for the transfer matrix formalism.

If we divide the whole lattice as vertical strips (see Figure 3.12), Eq. 3.19 can be rewritten as

$$h_n |\Psi_n\rangle + h_{n,n-1} |\Psi_{n-1}\rangle + h_{n,n+1} |\Psi_{n+1}\rangle = E |\Psi_n\rangle, \quad n = 1 \dots L \quad (3.20)$$

This can be further written as

$$|\Psi_{n+1}\rangle = h_{n,n+1}^{-1} ((E - h_n) |\Psi_n\rangle - h_{n,n-1} |\Psi_{n-1}\rangle) \quad (3.21)$$

Equivalently, in the matrix form, Eq. 3.21 looks like

$$\begin{pmatrix} |\Psi_{n+1}\rangle \\ |\Psi_n\rangle \end{pmatrix} = \begin{pmatrix} h_{n,n+1}^{-1} (E - h_n) & -h_{n,n+1}^{-1} h_{n,n-1} \\ 1 & 0 \end{pmatrix} \begin{pmatrix} |\Psi_n\rangle \\ |\Psi_{n-1}\rangle \end{pmatrix} = T_n \begin{pmatrix} |\Psi_n\rangle \\ |\Psi_{n-1}\rangle \end{pmatrix} \quad (3.22)$$

Thus given the initial value for Ψ_0 and Ψ_1 and energy E , one can iterate using Eq. 3.22 and get the wave function for any strip

$$\begin{pmatrix} |\Psi_{n+1}\rangle \\ |\Psi_n\rangle \end{pmatrix} = \left(\prod_{i=1}^n T_i \right) \begin{pmatrix} |\Psi_1\rangle \\ |\Psi_0\rangle \end{pmatrix} = M_n \begin{pmatrix} |\Psi_1\rangle \\ |\Psi_0\rangle \end{pmatrix} \quad (3.23)$$

By increasing the number of strips, the norm of the resulting matrix grows exponentially. It was proven by Valery Oseledec that $\lim_{n \rightarrow \infty} (M_n M_n^\dagger)^{1/2n}$ exists. Assuming the limiting matrix has M eigenvalues e^{γ_i} (the matrix is positive definite).

These γ_i s, called Lyapunov exponents (LEs), characterize the rate of the exponential growth. They come in pairs, which are opposite of one another. The largest LE determines the growth of the norm of an arbitrary vector multiplied by the matrices; the smallest positive LE (or opposite of the largest negative LE) determines the decay of the norm at far distance, the inverse of which represents the spatial extension of the wave function.

To calculate the largest LE is simple. One simply multiplies the matrices and keep track of the largest norm. To calculate the smallest positive LE is much more difficult. Direct numerical multiplication of matrices isn't possible, as the matrix elements grow rapidly and generate large round-off errors for the smallest positive LE. We used a method Giancarlo Benettin developed.[59] Briefly,

1. Start with D (dimension of the transfer matrix) normalized vectors $\mathbf{v}_i$.
2. Multiply them by l matrices from a random sequence.
3. Implement a Gram-Schmidt orthogonalization. Store the length of the new vectors $(d_k^{(i)})$ and normalize them to unity.
4. Multiply the next l matrices and continue the procedure.

The LEs are then obtained as

$$\gamma_i = \frac{1}{nl} \sum_{k=1}^n \log \left(d_k^{(i)} \right), \quad i = 1 \dots D \quad (3.24)$$

and the localization length is defined as the inverse of minimum positive LE:

$$\xi_M = \frac{1}{\gamma_{\min}} \quad (3.25)$$

A mathematica program that was used to calculate all the LEs using Giancarlo Benettin's method is attached in Appendix 3.8.8.

3.6.2 Renormalization Group Theory and Finite-size Scaling

The calculation of the LEs is costly. The computation complexity for our algorithm scales as $L \times M^3$, thus we are only able to calculate it for relatively small M . The actual localization length is $\lim_{M \rightarrow \infty} \xi_M$. In order to obtain this limit, we use idea of the renormalization group.[60] The scaling hypothesis here is that the dimensionless quantity $\Lambda_M = \xi_M/M$ depends only on $\xi(\alpha)/M$, and not on the parameters and M separately:

$$\Lambda_M = f\left(\frac{\xi(\alpha)}{M}\right) \quad (3.26)$$

where α is a composite parameter that includes all the descriptions of the system except its physical dimension. This includes the eigenvalue (or energy) and the strength of disorder. $\xi(\alpha)$ is the localization length in an infinite system. The function f may depend on dimensionality and on certain symmetries but is otherwise universal.

In practice, we calculate ξ_M for several M and the parameter α . We plot them all together on a log-log scale in terms of Λ_M vs. $1/M$. Then for each given α , we shift the corresponding data set horizontally so that all data overlap on the same universal curve f . If this is indeed the case, then our scaling hypothesis is correct, and we've obtained the localization length $\xi(\alpha)$ for all α , up to a constant. We can determine this constant, by using the fact that when M is very large (or when disorder is large and thus $\xi(\alpha)$ is small), $\xi_M \rightarrow \xi(\alpha)$ and $\lim_{x \rightarrow 0} f(x) = x$.

Figure 3.13 shows Λ_M vs. $1/M$ for a number of different combinations of M , s/t_0 , κg and E . Figure 3.14 shows the same data after the data collapse. It is clear that all data fit very well on a single universal curve.

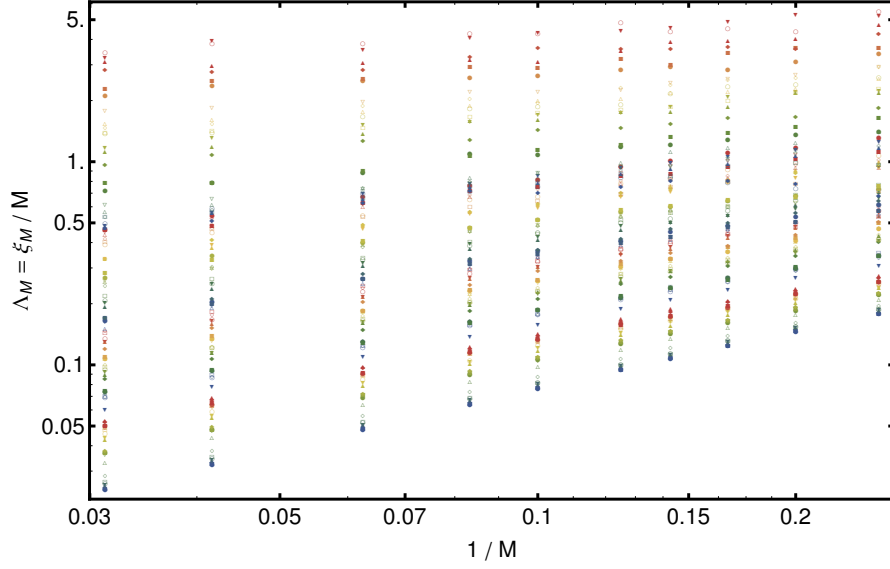


Figure 3.13: Λ_M vs. $1/M$ on log-log scale. Different color corresponds to different combination of s/t_0 , κg and E . We used free boundary condition in the calculation. Adjacent data set has large overlap in the $y(\Lambda_M)$ axis, which is essential for fitting $\xi(\alpha)$.

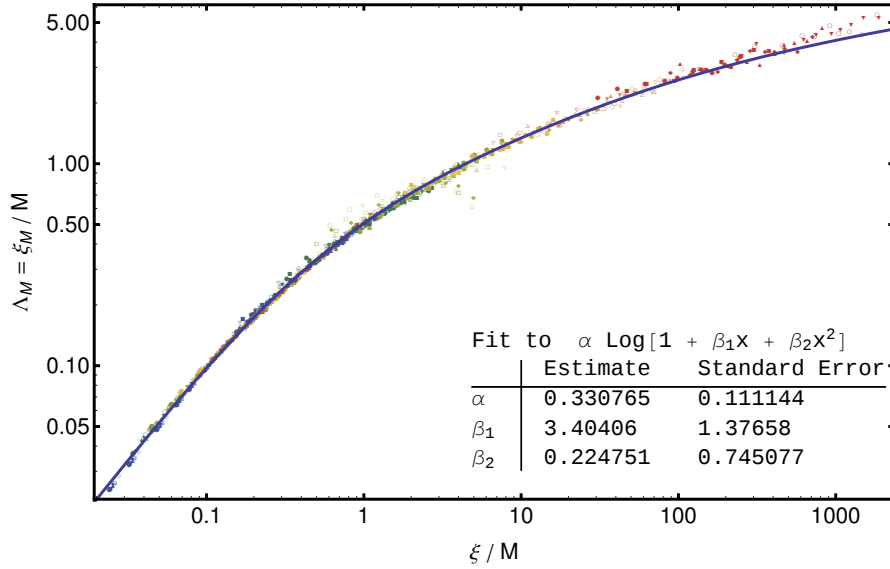


Figure 3.14: Λ_M vs ξ/M on log-log scale. The data used is exactly the same as in Figure 3.13, but with each data set α horizontally shifted by $\xi(\alpha)$.

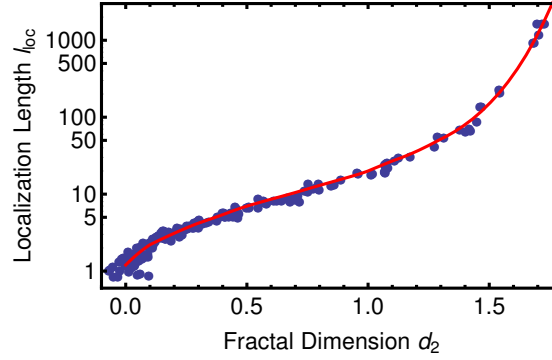


Figure 3.15: Localization length *vs.* fractal dimension in 2D superlattice. All data lies nicely on a single universal curve, which can be used to convert one into another.

3.6.3 Discussion

Figure 3.14 is very much the same as the one obtained in ref. [60] using Anderson model. This is not at all surprising since scaling laws only depends on dimensions and general symmetry of the interactions, not on the details of the interactions.

Now we go back to our original goal and see if the fractal dimension(d_2) and localization length (l_{loc}) is equivalent to each other. Figure 3.15 shows localization length calculated here compared with fractal dimension calculated in section 3.2, for 400 different combinations of disorder and energy. It is clear that all data lies on the same universal curve. This proves that d_2 and l_{loc} are really describing the same thing just in two different ways. To make it easier for comparison, we tabulate l_{loc} vs. d_2 values in Appendix 3.8.9.

At the high end, we notice that in 2D, there aren't any real completely delocalized states. The localization length keeps growing towards but never reaching the infinity when the fractal dimension approaches 2. But when fractal dimension is larger than 1.5, the localization length is so large > 100 that for all intents and purposes the wave function is almost delocalized.

At the low end, for a fractal dimension of 0.1, the coherent length is only twice the lattice constant; if the fractal dimension is 0.3, coherent length increases to 4; once the fractal dimension reaches 0.7, it increases to 10. In this case, even though the fractal dimension is still much smaller than 1.0, the wave function is already spread out quite a bit, though not yet extending over the entire superlattice. If electron transport through these states, we expect we should already see a noticeable improvement in transport efficiency.

3.6.4 Localization Length in 3D Superlattices

When we calculate the localization length in 3D, we slice the 3D crystal into 2D finite sheets, and calculate the wavefunction decay in the third direction (Figure 3.16c).

In the same method as in 2D, we use finite scaling to extrapolate localization length to an infinite lattice. However, the localization-delocalization transition happens at finite disorder in 3D. As a result, the “delocalization length” separates into two distinct branches (Figure 3.16 a): in the localization regime, Λ_M increases with $1/M$ as usual; in the delocalization regime, Λ_M decreases with $1/M$. When we implement the data collapsing to get true localization length, we only use data from the lower branch (Figure 3.16 b). The results are consistent with those in previous literatures on Anderson model.[60]

Finally we compare the localization length *vs.* fractal dimension we calculated previously (Figure 3.16d). Again, all data points lie on the same universal curve, no matter what their disorder is. However this curve is different from the same curve we obtained in 2D. At the same fractal dimension, the localization length is

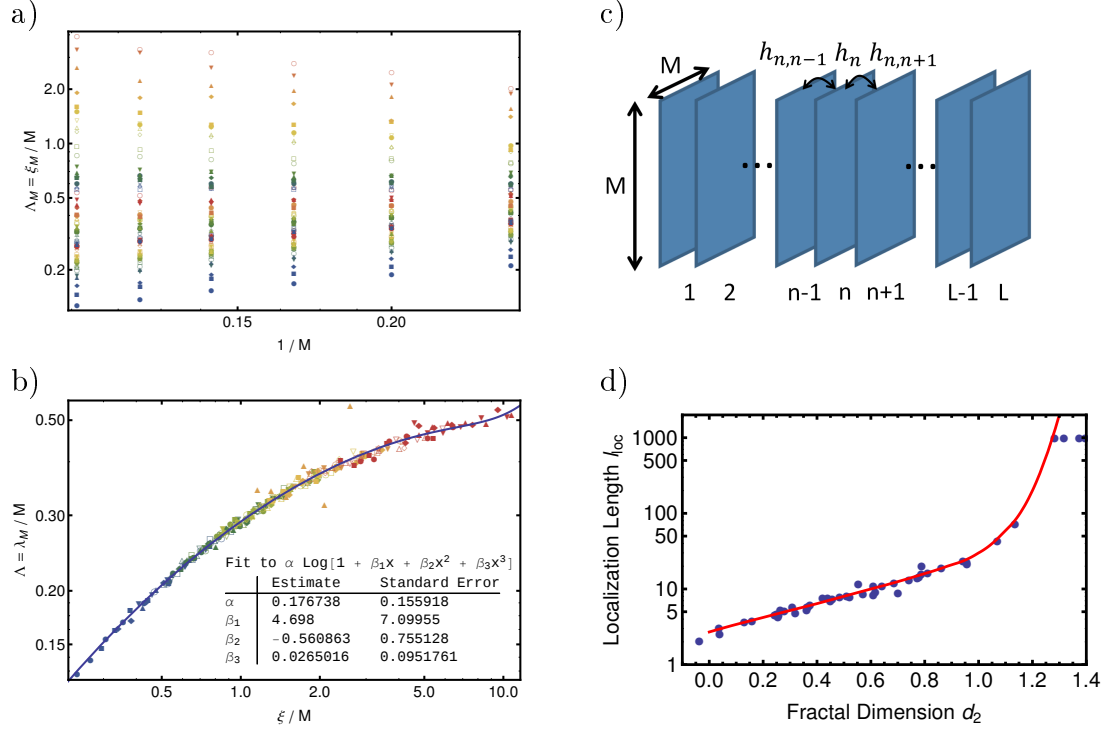


Figure 3.16: Localization lengths in 3D. (a) The uncollapsed data of Λ_M vs. $1/M$. (b) Λ_M vs. ξ/M after fitting. (c) Schematic of the transfer matrix formalism in 3D. (d) Localization vs. fractal dimension.

slightly larger in 3D than in 2D. Values are tabulated in Appendix 3.8.9.

3.7 Conclusion

We used a tight binding model with explicit modeling of on-site energy disorder and positional disorder to evaluate the existence of delocalized states in a nanocrystal solid. We obtain phase diagrams that show directly the critical disorder that eliminates delocalized transport, for several crystal structures. We used a one-band effective mass model to calculate the coupling energy. We found that in EDT-treated nanocrystal solids made of small PbSe nanocrystals, the disorder is marginal to allow coherent transport. For lead salt NCs, we also studied the

effect of inter-valley coupling, which does generally improve delocalization, but not enough to make a real difference with current synthetic capabilities. We also looked into the recently developed atomically coherent superlattice. The improved ordering is partly negated by their 2D nature and the limitation to the size of NCs used. We found the one to one correspondence between fractal dimension and localization length. It shows that even when the electronic state is not delocalized, its wave function might be “delocalized” enough for us to see the benefit of coherent transport.

In order to observe coherent transport through delocalized states, all the incoherent scattering should be reduced so that the mean free path due to incoherent scattering is larger than or at least comparable to the sample size. These include scattering from domain boundaries, scattering from thermal fluctuation of the lattice, and charge trapping in defects. Also, the Fermi level of carriers has to be within the mini-band for the transport to benefit from these delocalized states. If the mini-band is very narrow, it requires a significant amount of charge doping (more than one electron per dot). This will introduce strong electron-electron scattering. This is not captured in the current single particle model and will lower the mobility further.

Overall, we believe that with the right ligand for electronic coupling, infilling of the void space with smaller-bandgap semiconductors and proper passivation of surfaces, band-like transport is attainable.

3.8 Appendix

3.8.1 Random Close Packing

The random close-packed assembly is generated with force-biased algorithm.[37] The algorithm is not unlike blowing balloons in a box. It starts from a random distribution of particles in a simulation box. Each particle has an inner diameter and an outer diameter. The inner diameter is chosen so that the particles in the closest pair barely touch each other. The outer diameter is initially chosen to be a large number, and then progressively reduced in the rearrangement process. In each iteration, forces are calculated with each pair of particles that have intersecting outer spheres. The positions of all particles are then readjusted according to this force to reduce intersection. The new inner diameter is then recalculated, the outer diameter is reduced, and the progress goes on, until the inner and outer diameter are the same. The final positions of the particles is in random close-packing. The algorithm is effective and creates very dense packing close to the theoretical limit. Figure 3.17 shows the pair distribution function. The number of nearest neighbors is approximated as the cumulative pair distribution function at a very short distance (1.02).

3.8.2 Band Parameters for Cadmium Salts and Lead Salts

The band parameters used in the simulation are listed in Table 3.2.

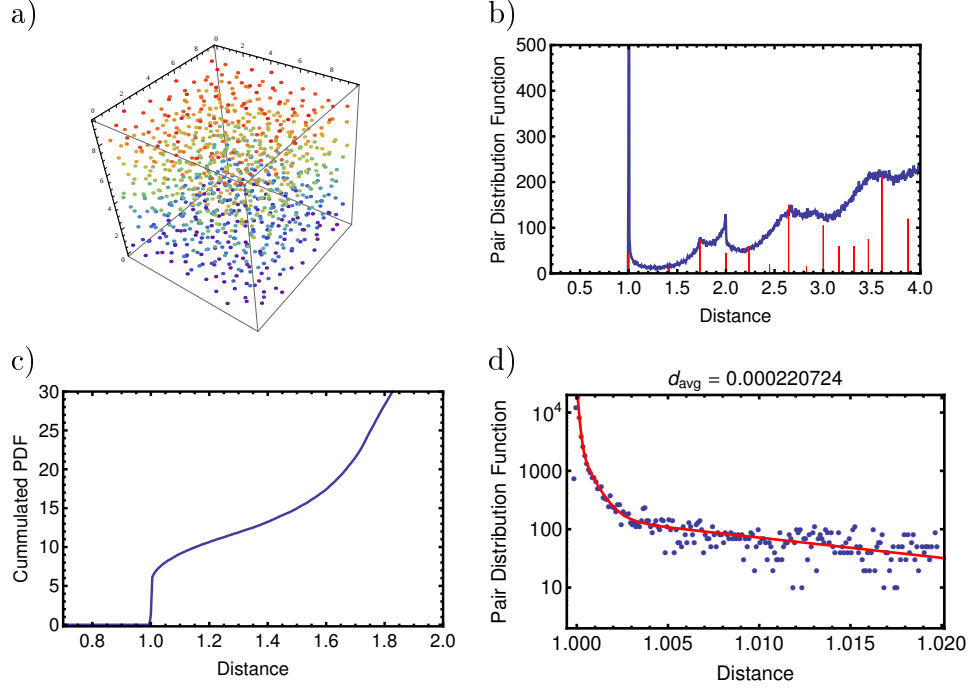


Figure 3.17: Characterization of random close packing. a) An example of 1000 identical spheres with diameter=1 packed in a cube of length 9.426986 with periodic boundary condition. b) Calculated pair distribution function (PDF). Red lines is PDF for a perfect fcc lattice. Notice there are sharp peaks at distance equal to 1.0, $1.74 = \sqrt{3}$ and 2.0. c) Cumulative PDF. The average total number of neighbors that are almost touching (within [1.00,1.01]) is around 6.5. The average total number of neighbors that are close (within [1.00,1.1]) is 9.1. d) PDF in log scale in the range [1.00,1.02].

	$E_g(\text{eV})$	$m_{avg,n}(m_0)$	$m_{avg,p}(m_0)$
PbS[61]	0.41	0.087	0.083
PbSe[61]	0.28	0.047	0.041
CdS[62]		0.18	
CdSe[63]		0.12	

Table 3.2: Effective mass used in the calculations

3.8.3 Dependence of Coupling Energy on the Value of V_{well}

To verify that the calculation result does not depend on the exact value of V_{well} , we change the value of V_{well} from 2.0eV to 6.0eV while keeping $m_{eff,C}V_{well}$ the

same, calculate f_2 , f_3 , and fit them to an exponential function $f_{2,3} = A_{2,3}e^{-\kappa_{2,3}d}$. The results are listed in Table 3.3. We can see that κ_2 , A_3 , and κ_3 are all almost independent of the V_{well} . A_2 does depend on the value of V_{well} , but it is clear that f_2 is consistently orders of magnitude smaller than f_3 , especially when one considers the much larger distance dependence.

$V_{well}(\text{eV})$	3.0	4.0	5.0	6.0
$A_2(\text{meV})$	3.3	1.8	0.93	0.38
$\kappa_2(\text{\AA}^{-1})$	0.81	0.82	0.83	0.84
$A_3(\text{meV})$	9.8	9.6	9.0	8.4
$\kappa_3(\text{\AA}^{-1})$	0.40	0.40	0.40	0.41

Table 3.3: Fitted exponential parameters for different potential well height

3.8.4 Valley Coupling Strength *vs.* Energy Splitting in a Single NC

The four valleys are completely symmetric. Therefore, the coupling strength between every two valleys should be equal in magnitude. The phase of the coupling is undetermined from symmetry arguments. Figure 3.18 lists two possible cases for the coupling matrices, and their corresponding eigenvalues for the different phases. The exact energy splitting depends on the value of the phase. But the total energy splitting between the highest and lowest energy states is consistently about 4 times the inter-valley coupling strength. From previous *ab-initio* calculations,[55, 56] we estimate that the total splitting for 4 nm PbSe nanocrystals is around 60meV, and therefore $V_{int} \approx 15 \text{ meV}$.

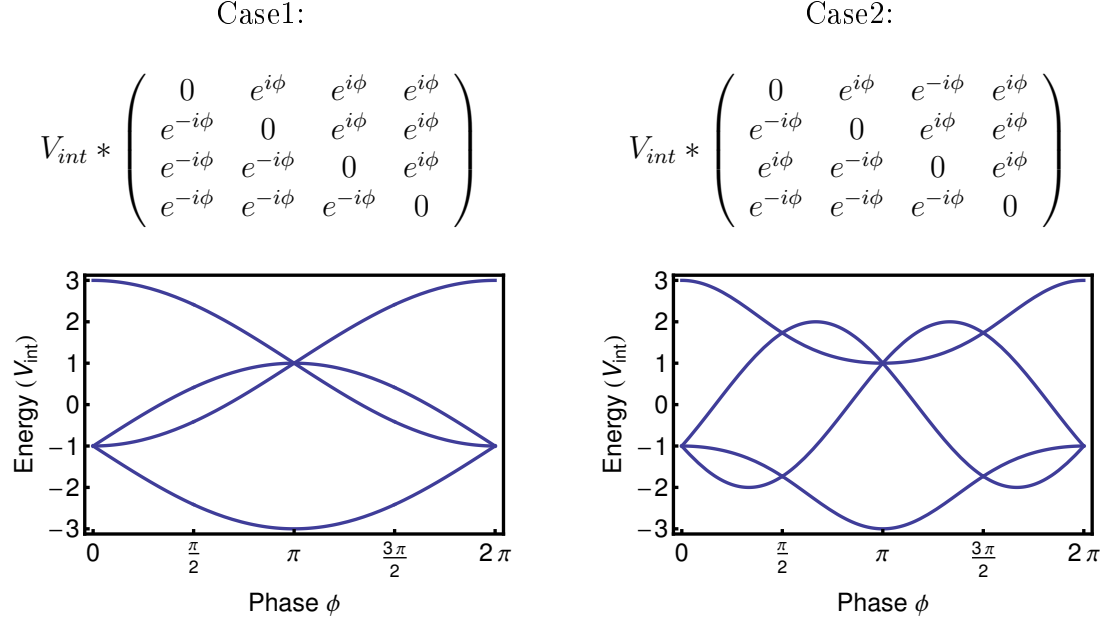


Figure 3.18: Energy level splitting due to inter-valley coupling for different coupling phase.

3.8.5 Comparison of Single-valley *vs.* Multi-valley Models in 2D Square Lattice, for Different Disorders

We've chosen three different disorder conditions, where either on-site energy disorder or positional disorder is predominant, or when the two are comparable. The corresponding disorder is plotted as red dots in the phase diagram of the single-valley model in Figure 3.19.

Table 3.4 summarizes the calculated results for single-valley and multi-valley models for different values of inter-valley coupling strength for $\alpha = 1.0$. Table 3.5 shows the same result but for $\alpha = 0.8$.

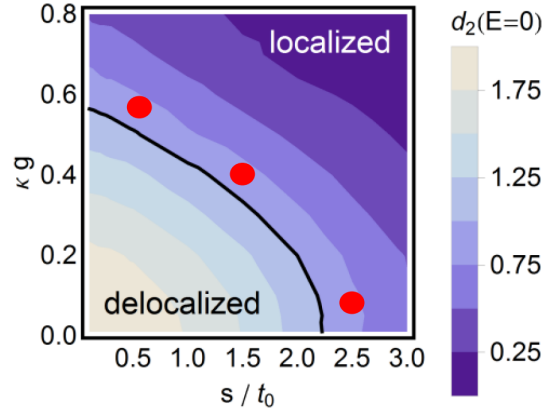


Figure 3.19: Visualization of the disorder parameters used in the calculations.

$\alpha = 1.0$	Single-valley	Multi-valley $V_{int}/t_0 = 0$	Multi-valley $V_{int}/t_0 = 1.0$	Multi-valley $V_{int}/t_0 = 2.0$
$s/t_0 = 0.5$	Max=0.84	Max=0.85	Max=0.83	Max=0.90
$\kappa g = 0.6$	Width=7.0	Width=7.0	Width=9.0	Width=15
$s/t_0 = 1.5$	Max=0.90	Max=0.90	Max=0.90	Max=0.95
$\kappa g = 0.4$	Width=8.8	Width=9.0	Width=12.5	Width=17
$s/t_0 = 0.5$	Max=0.83	Max=0.87	Max=0.82	Max=0.94
$\kappa g = 0.6$	Width=7.2	Width=6.3	Width=9.0	Width=15

Table 3.4: The maximum fractal dimension and full width half maximum of the band, for different disorders. ($\alpha = 1.0$, $\phi = 0$)

$\alpha = 0.8$	Single-valley	Multi-valley $V_{int}/t_0 = 0$	Multi-valley $V_{int}/t_0 = 1.0$	Multi-valley $V_{int}/t_0 = 2.0$
$s/t_0 = 0.5$ $\kappa g = 0.6$	Max=0.84 Width=7.0	Max=0.80 Width=16	Max=0.80 Width=8.0	Max=1.03 Width=10
$s/t_0 = 1.5$ $\kappa g = 0.4$	Max=0.90 Width=8.8	Max=0.90 Width=9.0	Max=1.26 Width=8.0	Max=1.28 Width=12
$s/t_0 = 0.5$ $\kappa g = 0.6$	Max=0.83 Width=7.2	Max=1.0 Width=8.0	Max=1.50 Width=7.0	Max=1.55 Width=10
$s/t_0 = 2.5$ $\kappa g = 0.6$				Max=0.60 Width=11
$s/t_0 = 1.5$ $\kappa g = 0.6$				Max=0.80 Width=10
$s/t_0 = 2.5$ $\kappa g = 0.4$				Max=1.06 Width=11

Table 3.5: The maximum fractal dimension and full width half maximum of the band, for different disorders. ($\alpha = 0.8$, $\phi = 0$)

3.8.6 Comparison of Single-valley *vs.* Multi-valley Models in 3D Cubic Lattice, for Different Disorders

Figure 3.20 shows the wave function delocalization for different valley coupling model (α). Figure 3.21 shows delocalization for different combination of on-site and structural disorder.

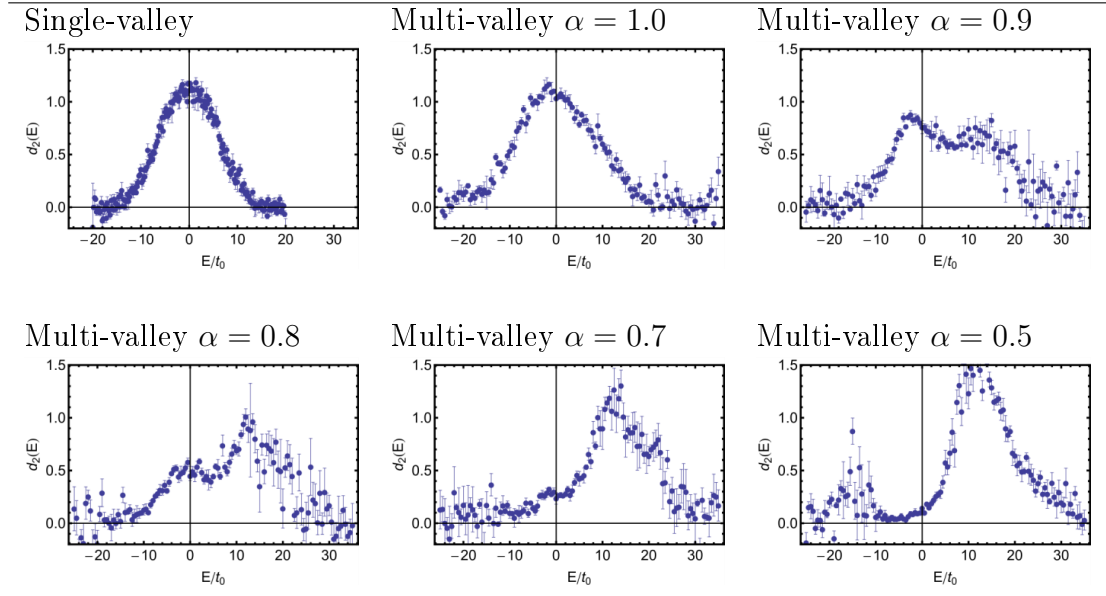


Figure 3.20: Comparison of fractal dimension d_2 with different coupling selectivity α . Parameters: $s/t_0 = 4.0$, $\kappa g = 1.0$, $V_{int} = 2.0$. $\alpha = 1.0$ corresponds to coupling only through the same valley; $\alpha = 0.5$ corresponds to equal coupling between all 4 valleys. It is clear that as α decreases, the “localization” band appears between $E = -10t_0$ to $10t_0$.

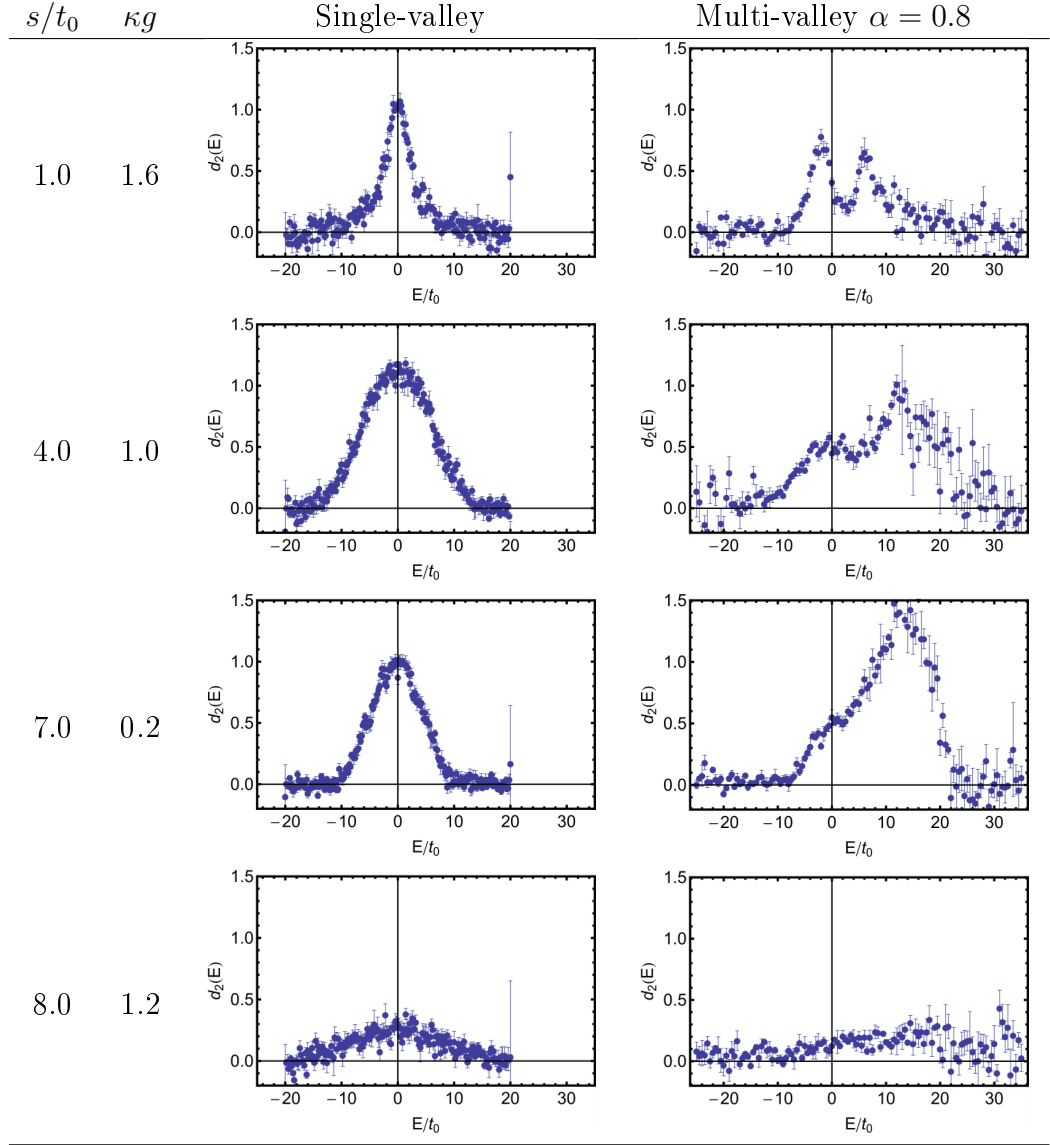


Figure 3.21: Comparison of fractal dimension d_2 with different disorders, for 3D simple cubic lattice. Parameters: $V_{int} = 2.0$. First three cases correspond to predominant positional disorder, intermediate case, and predominant on-site energy disorder; the last case corresponds to system that is close to current experiments.

3.8.7 Relative Orientation Between Valley and Bond

The orientation of the four valleys can be described using four vectors in the Cartesian coordinates $v_1 = [1, 1, 1]$, $v_2 = [1, -1, -1]$, $v_3 = [-1, -1, 1]$ and $v_4 =$

$[-1, 1, -1]$. Notice that due to the shape of the Brillouin zone, v_i is equivalent to $-v_i$. The difference between two valleys can always be represented as one and only one direction parallel to x, y or z axis. For example, $v_1 - (-v_2) = 2 * [1, 0, 0]$ parallel to x axis; $v_2 - (-v_3) = -2 * [0, 1, 0]$ parallel to y axis, etc. The relative orientation is summarized in Table 3.6.

	1	2	3	4
1	/	x	z	y
2	x	/	y	z
3	z	y	/	x
4	y	z	x	/

Table 3.6: Relative orientation between valleys

The direction of bonds in a simple cubic or simple square lattice is either x, y or z. Therefore, there are only two different cases: the relative orientation is either parallel ($V_{\alpha\beta,0}$) or perpendicular ($V_{\alpha\beta,90}$) to the bond direction.

3.8.8 Mathematica Program to Implement Giancarlo Genettin Method

Algorithm 3.1 Giancarlo Genettin Method

```
(*m: List of random matrices (l*n long) for multiplication
  l: number of multiplied matrices before orthonormalization
  n: number of orthonormalizations
*)
Lyapunov[m_,n_,l_]:=Module[{dim=Dimensions[m][[1]][[1]],
                             v,d,cnt,tmp},
  v=IdentityMatrix[dim];
  d=Array[0&,{dim,n}];
  cnt=0;
  Do[
    tmp=IdentityMatrix[dim];
    Do[cnt+=1;tmp=tmp.m[[cnt]],{i,1,l}];
    v=Map[(#.&tmp)&,v];
    Do[
      Do[v[[i]]=v[[i]]-v[[j]]*(v[[i]].v[[j]]),{j,1,i-1}];
      d[[i,k]]=Norm[v[[i]]];
      v[[i]]=v[[i]]/d[[i,k]];
    ,{i,1,dim}
  ],{k,1,n}];
  Table[Total[Log[d[[i]]]]/(n-1),{i,1,dim}]
]
```

3.8.9 Numerical values for localization length *vs.* fractal dimension in 2D and 3D

Fractal dimension d_2	Localization length l_{loc} (2D)	Localization length l_{loc} (3D)
0.0	1.2	2.7
0.1	2.2	3.4
0.2	3.1	4.2
0.3	4.2	5.2
0.4	5.4	6.4
0.5	7.0	8.0
0.6	8.6	10
0.7	10.5	12.5
0.8	13	16
0.9	16	21
1.0	20	30
1.1	27	60
1.2	36	200
1.3	52	inf
1.4	80	inf
1.5	150	inf
1.6	360	inf
1.7	1200	inf
1.8	6000	inf

Table 3.7: Interpolated numerical values for the localization length (l_{loc}) at different fractal dimensions (d_2) in 2D and 3D. Units: lattice constant.

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CHAPTER 4

EXCITON RELAXATION IN PBSE NANORODS

In the last two chapters, we've studied in theory the electronic states of 0D, 2D and superlattices. In this chapter, we'll use optical spectroscopy, and particularly transient absorption to study the exciton relaxation in 1D PbSe nanorods. The relaxation mechanism is used to differentiate models of the exciton states. Major results presented in the chapter on have been published in Ref [1].

4.1 Introduction

In the past decade, research in quasi-one-dimensional (1D) nanostructures has grown substantially. A number of overviews of nanowire (NW) and nanorod (NR) research have been published.[2, 3, 4] In a 1D structure the Coulomb interaction can act primarily through the host medium, so it will not be screened as effectively as in 0D (quantum dot) or 3D (bulk) materials. Thus, the transition from the limit of strong confinement to the limit of strong correlation can be investigated as the length of the nanostructure changes.

Coulomb interactions are manifested dramatically in carrier dynamics, as Auger processes are critically important in nanostructures.[5, 6] They present a major impediment to creation of optical gain,[7, 8] and are directly relevant to multiple-exciton generation (MEG).[9] Several studies of ultrafast electron dynamics in 1D or quasi-1D quantum-confined materials have been reported. For example, in small aspect ratio CdSe NRs, relaxation of high energy state is faster while lowest energy state population rises slower compared with QDs of same bandgap energy.[10] This was explained as due to the reduced energy level degeneracy caused

by the shape anisotropy. In NRs with larger aspect ratio, carrier thermalization happens in a dense manifold of high-energy states, and the behavior is similar to the bulk material.[11] CdSe NRs with different diameters but similar lengths were studied, and intraband relaxation was found to be faster in smaller rods,[12] which is consistent with hole-assisted Auger relaxation. Multi-exciton relaxation has been studied in CdSe NRs [13] and single-walled carbon nanotubes.[14] The relaxation was explained as a bimolecular Auger recombination in these 1D materials, in contrast to the three-body Auger relaxation found in quantum dots[15] and bulk materials.

There are few reports of anisotropic lead-salt nanostructures, mostly due to the difficulty of synthesizing anisotropic particles with isotropic (rock salt) crystal structure. Koh *et al.* recently reported a one-pot, catalyst-free synthesis of PbSe NRs with high optical quality.[16] The structures have diameter around 4 nm and are 20-30 nm long, so both dimensions are small compared to the exciton Bohr radius. A 4-band envelope-function calculation [17, 18] accounts well for the observed optical transitions. An important prediction of the theory is that the electrons and holes exist as tightly-bound excitons in PbSe NRs, in contrast to the situation in lead-salt quantum dots.[19] In terms of electron relaxation in 1D lead-salt structures, a theoretical treatment concludes that Auger recombination is forbidden for the lowest biexciton state.[20] On the other hand, Cunningham *et al.* reported that the efficiency of MEG in quasi-1D PbSe structures is significantly higher than that of PbSe quantum dots, and the MEG energy threshold is much lower.[21] This observation implies significant potential for NR solar cells, and increases the motivation to study carrier dynamics in lead-salt NRs.

Here, we report femtosecond optical studies of the relaxation of excitons in

PbSe nanorods with dimensions near $4\text{ nm} \times 20\text{ nm}$. Excitons created in excited 1Π states relax to the lowest exciton state in two stages in the first few picoseconds. The fast energy relaxation rate is similar to that found in PbSe quantum dots. Multiple excitons decay on the 100-ps time scale. The biexciton lifetime is found to be several times larger than that of quantum dots with the same energy gap, roughly as expected based on the volumes of the structures. However, the multi-exciton lifetimes scale as expected for a bimolecular recombination process, which is expected for tightly-bound excitons.

4.2 Material

We synthesized PbSe NRs using the one-pot reaction developed previously.[16] A typical transmission electron microscope (TEM) image is shown in Fig. 4.1(a). High-resolution TEM images (Supporting Information) confirm that the NRs are single-crystalline and grow along the (100) direction. We studied six NR samples (which we refer to as NR1 to NR6), with diameters ranging from 3.3 to 4.5 nm and lengths from 20 to 30 nm. These have lowest exciton transitions between 1100 and 1430 nm. It was difficult for us to grow high-quality NRs outside these ranges. Within each sample, there is about 10% variation in diameter and 25% in length. A PbSe quantum dot sample with lowest exciton transition near 1470 nm was also studied for comparison.

The theoretical exciton spectrum of a 4.5 nm x 28 nm PbSe NR is shown in Fig. 4.1(b). The single particle states are labeled as follows: $kX_{|n|}^{e,h}$ for the kth electron or hole level, with total z angular momentum equal to n, and angular momentum projection of the conduction (valence) band component of the wave function equal

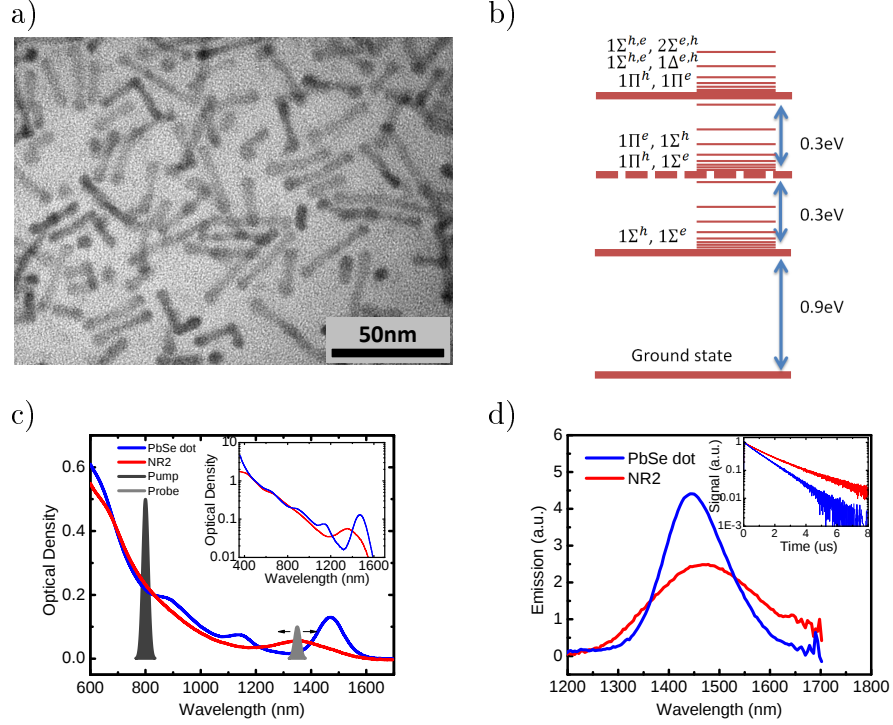


Figure 4.1: Structural and optical characterization of samples. (a) TEM image of nanorod sample NR2, which has dimensions $(4.5 \pm 0.6)\text{nm} \times (28 \pm 7)\text{nm}$. (b) Theoretical energy spectrum of sample NR2. Here $1\Pi - 1\Sigma$ states are dashed, as $1\Sigma - 1\Pi$ transition is optically forbidden. (c) Absorption spectrum of NR2 and a PbSe dot sample for comparison. Pump (800nm) and probe wavelengths (spanning from the blue side to the red side of the absorption peak) are shown. Inset: absorption spectra on semi-logarithmic scale, to show features at the high energy side. (d) Emission spectrum of NR2 and PbSe dot sample. Inset: fluorescence decays.

to $|m| = 0, 1, 2, \dots$ for $X = \Sigma, \Pi, \Delta, \dots$ [17] Due to strong electron-hole interaction, we draw the energy levels in terms of exciton states instead of single particle states. A typical absorption spectrum is shown in Fig. 4.1(c) along with the spectrum of the PbSe quantum dot sample for reference. The corresponding fluorescence spectra and decays are shown in Fig. 4.1(d). The fluorescence lifetime of the NRs is $1.7 \mu\text{s}$.

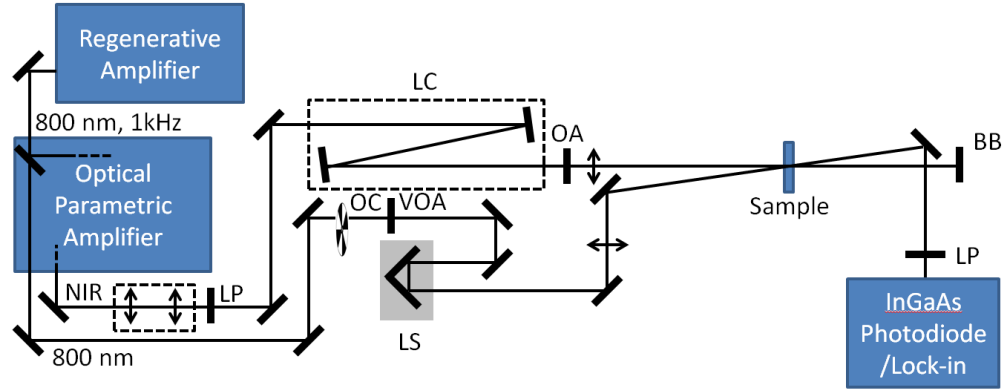


Figure 4.2: Transient absorption experimental setup. The regenerative amplifier outputs 800nm pulses, at 1kHz repetition rate and 1mJ/pulse. The FWHM pulse width is 130fs. 60% light is used to pump the optical parametric amplifier, which outputs near infrared beam (900nm-1550nm), typically around 30uJ/pulse, and used as the probe beam. The other 40% is used as the pump beam. Legend: $\uparrow$: focusing lens. LP: long pass filter. LC: optical length compensator. OC: optical chopper, synchronized with the laser pulse train. It blocks every alternative pulse. OA: optical attenuator. VOA: variable optical attenuator. LS: a corner cube mounted on a motorized linear stage. BB: beam block. The time resolution of the setup is 220 fs, determined by the cross-correlation of the 800-nm pump and $\sim$ 1500-nm probe pulses.

4.3 Results

Important relaxation processes occur on the 100-ps and 1-ps time scales, and was studied using standard time resolved transient absorption measurement. A typical experiment setup is shown in Figure 4.2.

We will begin with an overview of the experimental data and discussion of the dynamics on the 100-ps scale, which provide information on Auger relaxation of multiple ground-state excitons. Then, we will focus on the 1-ps time scale, which corresponds to energy relaxation within the electron or hole states. Qualitatively-similar results were obtained for all samples. Results obtained with sample NR2 ($(4.5 \pm 0.6)\text{nm} \times (28 \pm 7)\text{nm}$) will be discussed in detail, and then results obtained from all the samples will be summarized.

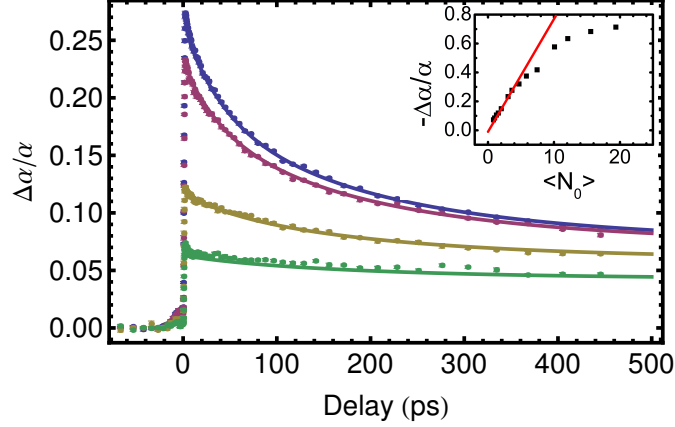


Figure 4.3: Saturated absorption traces for pump fluences corresponding to $\langle N_0 \rangle = 0.84, 1.6, 3.1, \text{ and } 3.6$, from bottom to top. α is the optical density at the probe wavelength, measured with the CW spectrometer, and $\Delta\alpha$ is the change in optical density due to the pump pulse. Solid lines are multi-exponential fits (see text), with $\tau_2 = 217 \text{ ps}$, $\tau_3 = 65 \text{ ps}$. Inset: signal magnitude measured at $t=3 \text{ ps}$ after the initial excitation, *versus* initial excitation ($\langle N_0 \rangle$). The line is the fit for low excitation.

4.3.1 Multi-exciton dynamics

The saturated-absorption traces obtained by excitation at 800 nm and probing the lowest exciton transition (Fig. 4.3) exhibit features that are familiar from work on quantum dots,[22, 23, 24] and are qualitatively similar to data presented in the study of MEG in 1D structures.[21] With initial excitation $\langle N_0 \rangle$ below one electron-hole pair per NR, the trace shows negligible change on the time scale of the measurement (500 ps), as expected from the microsecond population decay observed in fluorescence. As the pump fluence increases, faster decay components appear progressively, which correspond to discrete multi-exciton relaxation due to Auger recombination.

Modeling of the exciton dynamics follows the approach used for quantum dots.[22, 15] Since the excitons are created by photons with energy lower than twice the energy gap, MEG does not occur, and the excitation probability satisfies

the Poisson distribution: the probability that a NR has n excitons at $t = 0$ is

$$P_n(t = 0) = \frac{\langle N_0 \rangle^n}{n!} e^{-\langle N_0 \rangle}. \quad (4.1)$$

The excitons decay to the lowest state within a few picoseconds (this will be shown in the next section). From that point on, the exciton population distribution follows a cascade model:

$$\frac{dP_n(t)}{dt} = -\frac{P_n(t)}{\tau_n} + \frac{P_{n+1}(t)}{\tau_{n+1}} \quad (4.2)$$

$$\langle N(t) \rangle = \sum_{n=1} n P_n(t) \quad (4.3)$$

where τ_n is the n -exciton lifetime. The initial average population can be calculated as $\langle N_0 \rangle = j_p \sigma$, where j_p is the pump fluence per pulse, and σ is the absorption cross-section at the excitation wavelength. We calculated σ following previous work on PbSe quantum dots,[25] assuming that at high energy (3.1eV), NRs and quantum dots both behave like bulk material and thus have the same cross-section per unit volume. By scaling from the measured absorption at 400 nm and 800 nm, we obtained the cross-section at 800 nm, the excitation wavelength. Experimentally, the absorption spectra of the NRs and quantum dots do not match exactly at high energy (Fig. 4.1(c) inset), and this introduces uncertainty into our modeling. To reflect this, along with uncertainty in measurements of the pulse fluence, we treated the cross-section as a fitting parameter. The best-fit value of this parameter was always within 25% of the nominal cross-section, which indicates that the original assumption is reasonable. The effect of inhomogeneous excitation across the sample due to absorption was also considered in the model (see Supplementary Information). The saturated absorption signal 3 ps after the pump pulse varies

linearly with excitation intensity up to $\langle N_0 \rangle \sim 5$ (inset of Fig. 4.3), as expected based on similar results obtained with quantum dots. [22, 8] This enabled us to directly correlate the measured signal to the number of excitons in the NR, and ensured valid analysis.

By solving Eqn. 4.2 with the initial condition of Eqn. 4.1, we obtain the time-dependent exciton population. The parameters in the model are the absorption cross-section and the multi-exciton lifetimes τ_n , ($n = 1...5$). In solving Eqn. 4.2, higher exciton states ($n > 5$) were neglected, due to their short expected lifetimes and small probabilities of being excited initially.

For each sample and each probe wavelength, a global fit to the experimental data recorded for all excitation levels was performed. The best-fit curves (solid lines in Fig. 4.3) agree well with the data. The biexciton lifetime extracted from the fit $\tau_2 = 210 \pm 40 ps$, while the triexciton lifetime $\tau_3 = 64 \pm 7 ps$. The uncertainties in the inferred values of τ_4 and τ_5 are large, and we do not attach significance to those lifetimes.

Previous work on Auger recombination in quantum dots found that the biexciton lifetime is proportional to volume.[26] A study of CdSe NRs similarly found that the biexciton lifetime is linearly proportional to the NR length, for fixed diameter.[13] However, the lifetime is smaller than that of a quantum dot with the same volume. The biexciton lifetimes of our samples are summarized in Fig. 4.4. The large variations in the diameter and length of our NRs translates into large uncertainties in the volume, which hinders comparison to the trends observed in the prior work. We do not find systematic variation of the lifetime with volume, nor with energy gap. On the other hand, the biexciton lifetimes of the NRs are 3 to 4 times longer than those of the quantum dot sample with similar energy gap,

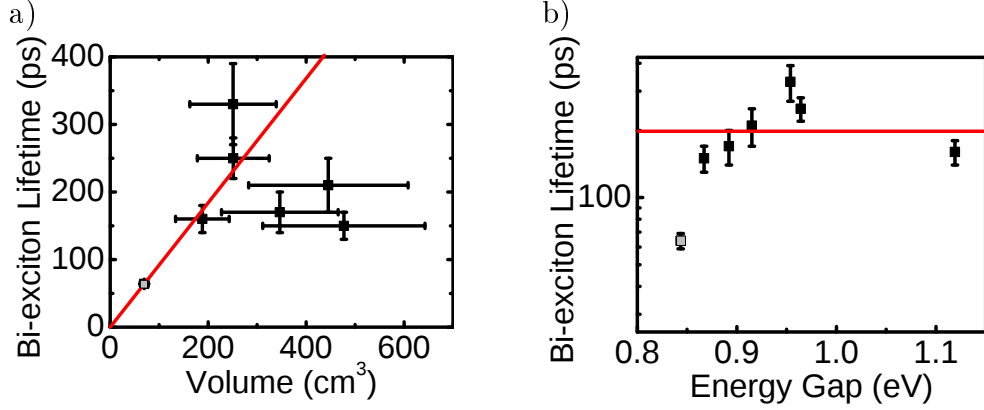


Figure 4.4: Biexciton lifetimes. (a) Bi-exciton lifetime *vs* volume. (b) Bi-exciton lifetime *vs* bandgap. The gray square is for the quantum dot sample; the red lines are to guide the eye.

which is roughly expected based on the volume of the structures. This contrasts with the results of Cunningham *et al.*, [21] who found similar biexciton lifetimes in quantum dots and 1D structures.

The ratio of multiexciton lifetimes can shed light on the nature of the charge-carrier states in nanostructures. For a nanocrystal with N electrons and N holes (independent charges model), $\tau_N^{-1} \propto N^2(N-1)$. The scaling factor is the product of the number of all possible conduction-to-valence band transitions (N^2) and the number of carriers that can accept the extra energy ($N-1$). In this case, $\tau_2/\tau_3 = 4.5$, which was confirmed in a study of PbSe quantum dots.[15] If the electron and hole are highly-correlated and form an exciton, the relaxation should be bimolecular, and the lifetimes should scale as $\tau_N^{-1} \propto N(N-1)$, in which case $\tau_2/\tau_3 = 3$. However, measurements of CdSe NRs[13] and carbon nanotubes[14] both found $\tau_2/\tau_3 = 1.5$. The results were explained as bimolecular recombination, but the analysis was not carried out in the small- N limit ($N = 2-3$). The different scaling law could be a consequence of specific band structure. For example, the small degeneracy of lowest exciton states in CdSe could result in triexcitons that

contain carriers in states of other symmetries. In this case, the triexciton lifetime is likely to be longer, due to reduced probability of interband transitions of states with different symmetries. This would reduce the ratio τ_2/τ_3 . [15]

Bartnik's theory predicts that the electron and hole form tightly-bound excitons in PbSe NRs, [17] so bimolecular scaling would be expected. We find $\tau_2/\tau_3 = 3.3 \pm 0.3$, in good agreement with the bimolecular model of multi-exciton recombination. The aspect ratios of our samples range from 5 to 7. In the case of CdSe NRs [13], the transition from 0D to 1D corresponds to an aspect ratio of 8. However, lead-salt materials may well have a different threshold for the transition from 0D to 1D. Experiments on PbSe NRs with a wider range of aspect ratios would be helpful for clarifying this point.

4.3.2 Energy Relaxation

We now turn to the first few picoseconds of the saturated-absorption traces obtained with excitation at 800 nm, which provide information about the energy relaxation of hot excitons. For a NR with lowest transition at 1350 nm, the $1\Pi_{3/2}^h \rightarrow 1\Pi_{3/2}^e$ and $1\Pi_{1/2}^h \rightarrow 1\Pi_{1/2}^e$ transitions (Fig. 4.1(b)) are predicted to be near 815 nm. [17] The $1\Sigma_{1/2}^{h,e} \rightarrow 1\Delta_{5/2}^{e,h}$, $1\Delta_{3/2}^{e,h}$, $2\Sigma_{1/2}^{e,h}$ transitions have approximately the same energy, but much weaker oscillator strength. Thus, excitation at 800 nm should only produce NRs with carriers in the 1Π states.

Measurements of the quantum dot sample are shown in the left panel of Fig. 4.5 for reference, and results from the NRs are shown in the right panel. Different lines correspond to different excitation fluences. The probe wavelength is 1414 nm for the NRs, on the low-energy side of the lowest exciton transition.

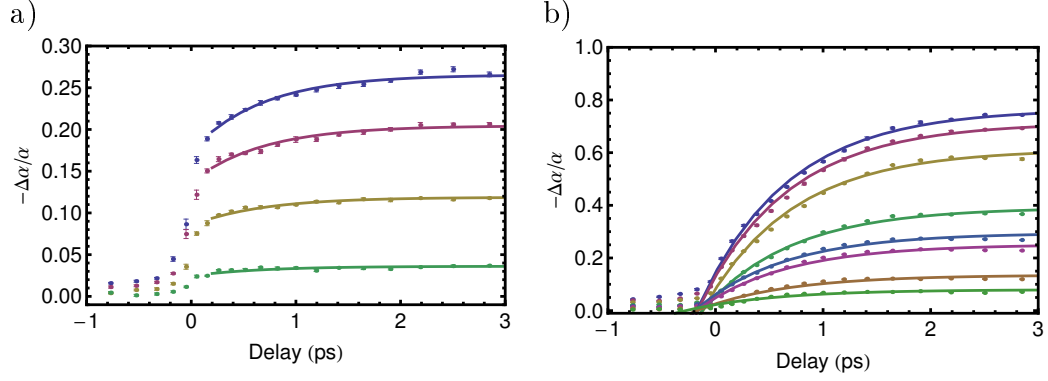


Figure 4.5: Rising edge of TA for different pump fluence. Left: quantum dot probed at 1470 nm, $\langle N_0 \rangle = 0.7, \dots, 3.3$, from bottom to top; Right: NR2 probed at 1414 nm, $\langle N_0 \rangle = 0.8, \dots, 25$. Due to a much larger absorption cross-section for NR, it's easier to probe higher excitation states in NR without any sign of sample damage.

The data from the quantum dots exhibit an instrument-limited rise time, as reported for previous measurements of intraband electron relaxation in PbSe quantum dots.[24] The rise of the population on the time scale of the pump pulse suggests that the pump and probe transitions have an energy level in common. The 800-nm excitation is not resonant with any particular excited states in this quantum dot. According to the 4-band envelope function calculation, a PbSe quantum dot with lowest transition at 1470 nm has $1p_h \rightarrow 1p_e$ transition near 970 nm.[19] It also has $1d_h \rightarrow 1s_e$ and $1s_h \rightarrow 1d_e$ transitions around 920 nm. Although the oscillator strengths for $s_h(d_h) \rightarrow d_e(s_e)$ transitions are small, they are closer to the excitation wavelength and thus contribute the instantaneous rising part of the transient-absorption traces. The instrument-limited rise is followed by the population increase that is attributed to the intraband relaxation in the quantum dots ($d_e \rightarrow s_e$, $d_h \rightarrow s_h$). In contrast, the signals from the NR sample exhibit only a well-resolved rise, which we attribute to population relaxing to the lowest manifolds of electron and hole states. By fitting traces from the same sample at different excitation fluences, a time constant of ~ 500 fs is inferred (Fig. 4.5).

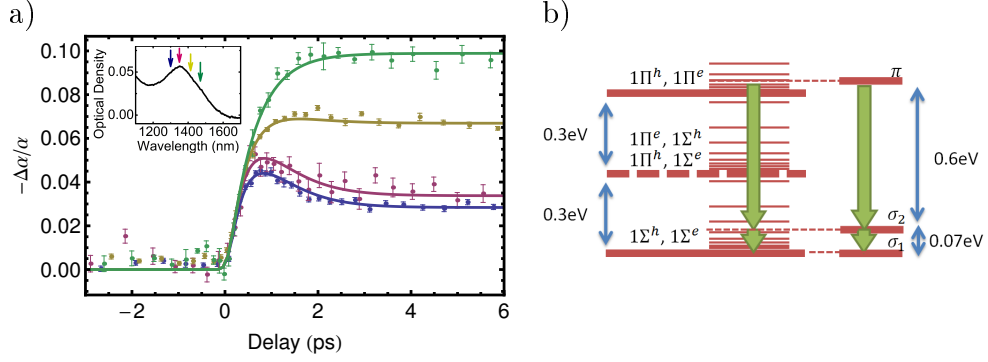


Figure 4.6: (a) Rising edge of transient absorption of sample NR2 at 1300 nm, 1350 nm, 1414 nm, 1470 nm. Pump wavelength 800 nm, $\langle N \rangle \approx 0.6$. Solid lines are fits to a two-stage cascade model with $\tau_a = \tau_b = 0.53$ ps (see text for details). Inset: absorption spectrum with probe wavelengths indicated. (b) Schematic of three-level system. π is a state in higher manifold; σ_2 is an intermediate state in the lowest manifold; and σ_1 is the lowest exciton state.

After the initial 500-fs rise, the transient-absorption traces depend on the probe wavelength (Fig. 4.6(a)). On the high-energy side of the lowest transition, the signal reaches at peak at a delay near 1 ps, and then decays to a lower level over the next few picoseconds. On the low-energy side of the transition, the trace continues to rise. At all probe wavelengths, a quasi-steady state is reached at ~ 3 ps. This indicates that the energy relaxation is a multi-step process, consistent with the energy spectrum of 1D structures. The strong confinement in the transverse direction produces manifolds of 1D exciton states (see Fig. 4.6 (b)). The initial component corresponds to the relaxation of excitons from the initial excited exciton state to the the ground exciton manifold. The later component comes from the relaxation within this dense energy manifold. Relaxation within the ground exciton manifold was studied in CdSe NRs.[11]

To quantify the energy relaxation, we introduce an approximate three-level model, with a high energy state (π) that corresponds to the photoexcited exciton; an intermediate state (σ_2) in the lowest manifold of states; and the lowest exci-

ton state (σ_1). Here π and σ_2 should be considered as groups of closely-spaced states. The energy difference between σ_1 and σ_2 is taken to be the energy difference between the probe wavelengths of 1300 nm and 1414 nm, 70 meV. The relaxation sequence is $\pi \xrightarrow{\tau_b} \sigma_2 \xrightarrow{\tau_a} \sigma_1$. Due to inhomogeneous broadening, the transient-absorption signal will have contributions from both σ_1 and σ_2 , but σ_2 will contribute more on the high-energy side, while σ_1 will contribute more on the low-energy side. The temporal instrument response was assumed to be a Gaussian with FWHM equals 220fs and incorporated in the fitting procedure. The best-fit traces are shown in Fig. 4.6 as the solid lines. The best fit is obtained with τ_a and τ_b equal to 0.53 ps.

Admittedly, this model is crude, and neglects detailed description of the dynamics between states in the same manifold. Due to limited signal to noise ratio, it is very hard to distinguish multiple components. Nevertheless, this model still provides useful information. The fact that τ_a and τ_b are similar means that the corresponding energy relaxation rates are very different. $\tau_b = 0.53\text{ps}$ implies an exciton energy relaxation rate of 1.1 eV/ps. If the electron and hole relax independently, the energy relaxation rate for each carrier would be 0.6 eV/ps. For comparison, the energy relaxation rate for the electron ranges from 0.15 to 1.0 eV/ps for PbSe quantum dots with diameters between 3.0 nm and 5.0 nm.[27] The comparable rates suggest that when carriers are in the high-energy manifold, they cool in the same way as in quantum dots: the electron and hole cool independently and they are not tightly bound. On the other hand, $\tau_a = 0.53\text{ps}$ implies an energy relaxation rate about 0.13 eV/ps. The reduced rate could be due to reduced density of possible final states as carriers relax to the band edge. In addition, the electrons and holes are more likely to be bound into excitons when they are sufficiently cold. Interaction between excitons and polar optical phonons is weak,[28, 29] and this

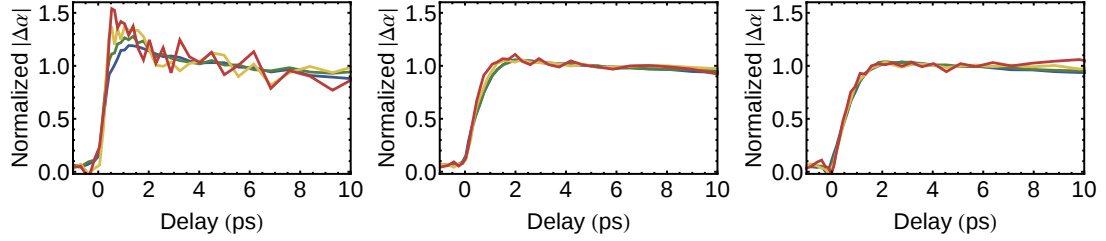


Figure 4.7: Normalized rising edge at different probe wavelength (1350 nm, 1414 nm, 1470 nm), with different pump fluence, corresponding to $\langle N \rangle = 3.3$ (blue), 2.8 (green), 1.4 (yellow), 0.8 (red). The traces are normalized to their values at long time (3 ps) for comparison.

would further reduce the cooling rate.

Finally, we find that the initial stage of relaxation depends on excitation fluence. Fig. 4.7 plots the rising edge with different pump fluence, at different probe wavelengths. The traces are normalized to their values at 3 ps to highlight the initial relaxation. Traces with different pump fluence overlap very well from 3 ps to 6 ps, which shows that the effect of Auger recombination due to different numbers of excitons is not present on this time scale. The rise in the ground-exciton population is faster at lower excitation levels. The trend is weaker on the low-energy side of the transition, and stronger on the high-energy side of the transition. These measurements suggest that multi-exciton states cool slower than single-exciton states. However, other explanations, such as hot-exciton induced Stark effect, could yield similar results.[30, 31] More detailed understanding of exciton interaction is needed here to give a definite explanation.

4.4 Discussion

We find that Auger relaxation is 3 to 4 times slower in NRs compared to quantum dots with the same energy gap. This is what one would expect due to the increased

volume, and thus reduced exciton density. Rupasov predicted theoretically that Auger recombination for the ground biexciton state is forbidden, and therefore should be strongly suppressed,[20] which is clearly not observed here. Our results also differ from those of Cunningham *et al.*, who found that nanorods and quantum dots have similar biexciton lifetime.[21] The structures they studied were quasi-1D hyperbranched structures, which could be a reason for the discrepancy. A reduced Auger rate should be beneficial in applications to lasing. This has been demonstrated with CdSe nanostructures.[32, 13] The energy-loss rate of single excited excitons in PbSe NRs is comparable to the rate in quantum dots. For MEG to be efficient, the energy relaxation of single excitons should be slower than the Coulomb scattering between single and multi-exciton states.[29] Our observation of slower Auger relaxation in nanorods (for similar values of photon energy in units of the energy gap) and similar energy-loss rate would predict a lower MEG rate in NRs. We suggest that the apparent asymmetry between Auger recombination and MEG is a consequence of the densities of states. In Auger recombination, the biexciton density of states is not relevant because the biexciton is the initial state. In MEG, the biexciton density of states is a crucial factor, regardless of the precise mechanism. For impact ionization,[33] the number of final states increases, while with coherent coupling of single and multi-exciton states,[31, 29, 34] the decoherence of multi-exciton states becomes quicker. Considering the exciton moving in 1D, the total number of exciton states is proportional to the length of the NR. The density of states for the biexciton (if we neglect their interaction) would be a convolution of two single-exciton densities of states, and therefore proportional to the square of length, much faster than the rise for single exciton states. This argument doesn't necessarily mean that the longer the wire, and higher the MEG efficiency. Momentum conservation, especially at high energy, would also limit the

effective number of states that actually undergo MEG. More studies are needed to find the optimum size and dimensionality that would result in the highest MEG efficiency.

4.5 Conclusion

We described measurements of Auger relaxation of multiple excitons, and intraband energy relaxation of charge carriers in PbSe nanorods. The biexciton lifetime of a nanorod is about the same as that of a quantum dot of the same volume, but is much larger than that of a quantum dot with same energy gap. The multi-exciton lifetimes scale approximately as expected for tightly-bound excitons, which are expected in these 1D structures. The intraband energy relaxation of excited excitons proceeds in two stages: the 1Π to 1Σ relaxation has a 500-fs time constant, and this is followed by additional slower energy relaxation within the manifold of 1Σ states. These results will be important to future applications of lead-salt nanorods in light emitters and photovoltaics, among others.

4.6 Methods

Chemicals. Selenium pellets (Aldrich, <5mm, 99.999%), tris(diethylamino)phosphine (TDP, Aldrich, 97%), lead(II) oxide (PbO, Aldrich, 99.9%), oleic acid (OA, Aldrich, 90%), 1-octadecene (ODE, Aldrich, 90%).

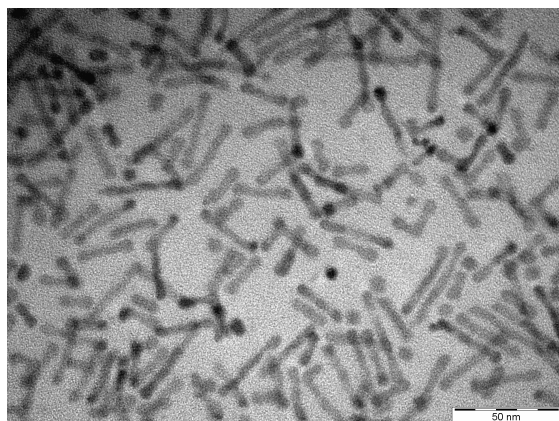
PbSe NR Synthesis. The synthesis follows the procedure in Koh *et al.*'s paper.[16] The selenium precursor is prepared by dissolving selenium pellets (.79 g, 10 mmol) into TDP (10 mL) overnight, forming a 1 M solution of TDPSe. The

synthesis is performed using a standard Schlenk-line. PbO (.22g, 1 mmol), oleic acid (1 mL, ~3 mmol), ODE (5 mL) are added to the reaction flask. The solution is vacuumed at <200 mTorr followed by N_2 gas under rapid stirring. This process is repeated three times before the solution is heated to 110 °C. The solution is again vacuumed for 3 minutes twice to get rid of water produced in the reaction. The solution is then heated to the desired injection temperature (170 °C in a typical synthesis) and allowed to stabilize. The 1 M TDPSe solution (3 mL, 3 mmol Se) prepared prior to the synthesis is obtained from the glovebox, and quickly injected into the reaction flask. Upon injection, the temperature of the solution drops 10-20 °C below the injection temperature. The heating element is manually adjusted to keep the solution at a near constant temperature for a desired reaction time (3-5 minutes). Over the course of the reaction it is typical for the temperature to fluctuate within a 5 °C range. After the reaction, the flask is quickly placed in an ice bath while being stirred until the solution temperature reaches room temperature. 5 mL of hexane is then injected into the solution. The solution is precipitated by acetone and ethanol. The precipitated nanorod is isolated by centrifugation at 2500 rpm for 5 mins and redissolved in toluene and placed into the glovebox.

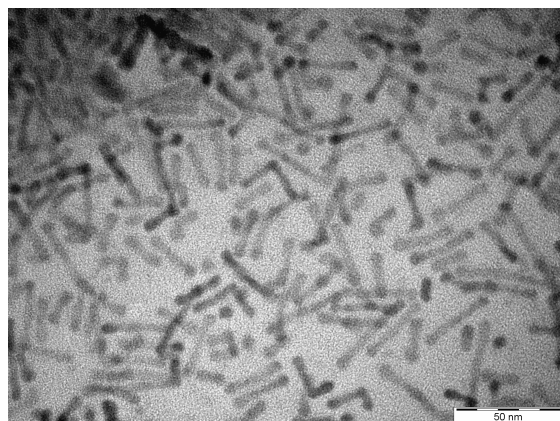
Sample Preparation. Samples were prepared by suspending PbSe NRs in tetrachloroethylene. The samples were sealed in an air-free environment and removed just before the optical experiments. A 3 mm×3 mm cuvette was used, with the concentration chosen to keep the optical density less than 0.3 at the excitation wavelengths. Experiments were performed with both static and flowing samples, and nearly-identical results were obtained. Results presented were obtained without flowing the sample, which yielded better signal-to-noise ratios.

4.7 Appendix

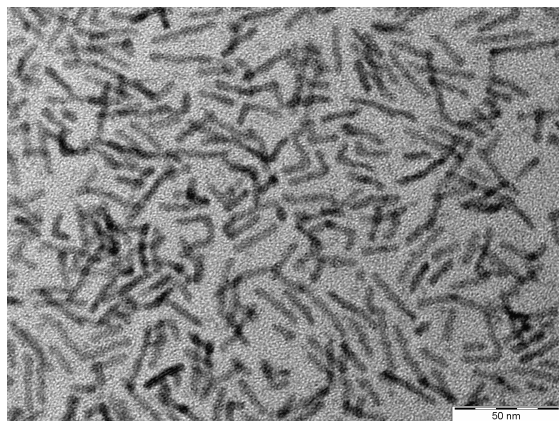
4.7.1 TEM pictures of all samples studied



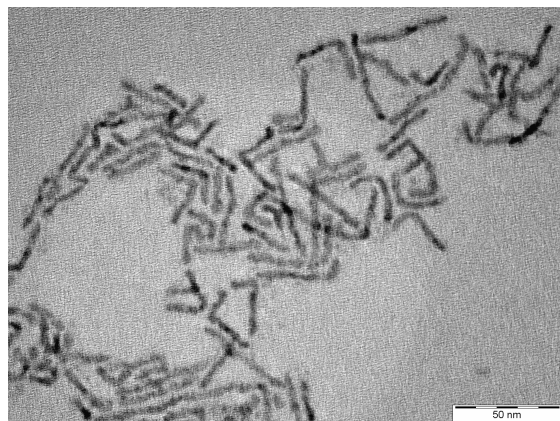
NR1



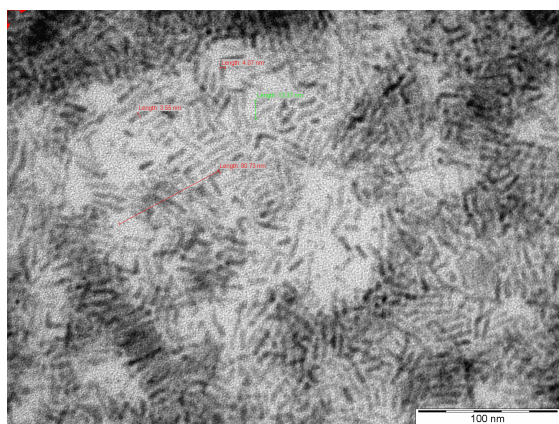
NR2



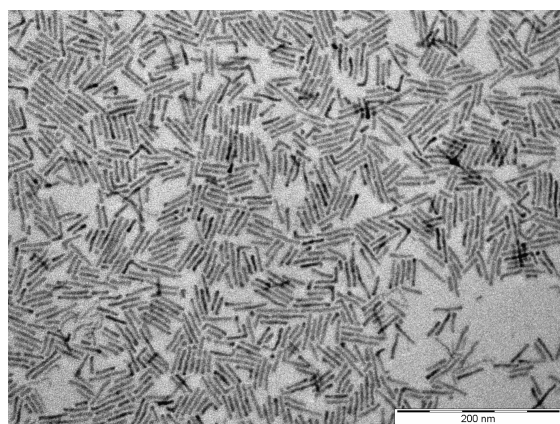
NR3



NR4



NR5



NR6

Table 4.1: TEM pictures of Sample NR1-NR6

4.7.2 HRTEM of sample NR2

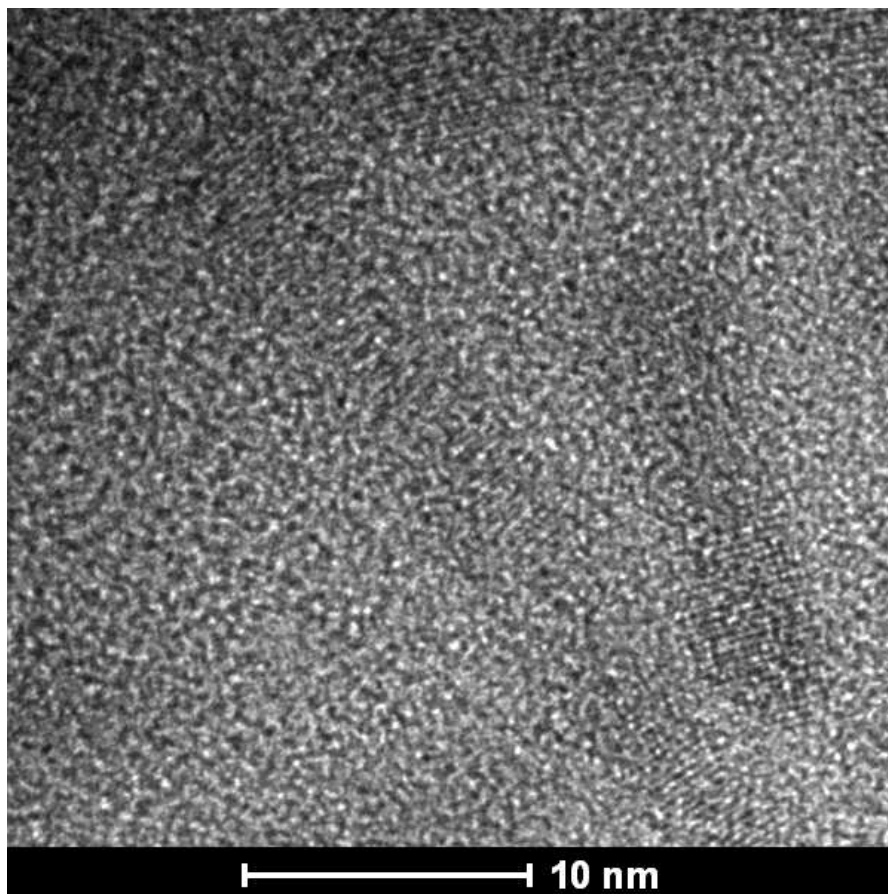


Figure 4.8: HRTEM picture of sample NR2 showing 001 crystal lattice plane.

4.7.3 Ensemble absorption spectra of all NR samples

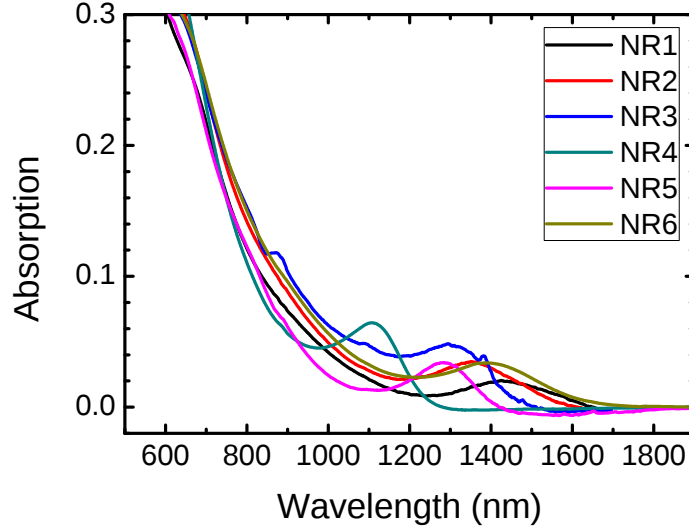


Figure 4.9: Absorption spectrum of all nanorod samples (NR1-NR6) studied. All spectra are normalized at 400nm.

4.7.4 Effect of uneven excitation on modeling

Even with an optical density of 0.3, the light intensity at the front and the back side of the cuvette would vary by a factor of 2 across the sample. The difference is accounted for in our model. We consider $\langle N_0 \rangle$ as position dependent by Beer's Law:

$$\langle N_0(x) \rangle = \langle N_0(x=0) \rangle \times e^{-\ln(10)ODx}, \quad x \in (0, 1)$$

Then the average number of excitons across the sample at any time is calculated as the integral

$$\langle N(t) \rangle = \int_0^1 \langle N(x, t) \rangle dx$$

, where $\langle N(x, t) \rangle$ is the number of excitons at time t by assuming the initial population is $\langle N_0(x) \rangle$. The $\langle N(t) \rangle$ was fitted to our data.

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CHAPTER 5

LEAD SALT NANOCRYSTAL FINE STRUCTURE

5.1 Introduction

Lead salt nanocrystals (NCs), thanks to their ideal bandgap energy, have been studied extensively in optoelectronic device applications. However, their detailed electronic structure, though very important, is still not clear. Low temperature photoluminescence of lead salt NCs has been reported multiple times.[1, 2, 3] It was found that there are two states, in thermal equilibrium with each other, that are responsible for the low temperature emission. One of the states, prominent at room temperature, is the ordinary exciton state, which is also the state responsible for the absorption. The nature of the other state is not clear. It is construed as either a defect state, or a dark exciton state, split by spin-orbit coupling or inter-valley coupling.

Similar temperature dependence of photoluminescence has also been observed in cadmium salt NCs, but with more prominent low energy peak. The low energy peak was assigned to defect states at the surface.[4, 5, 6] Recently a new model was developed, which involved only one surface trap state instead of an energetically broad distribution of midgap defect states.[7, 8] The broad emission spectrum from the defect state was explained as the natural result of large electron phonon coupling. The initial charge trapping process was explained in terms of semiclassical electron transfer theory.

In this chapter, we will use a number of optical spectroscopy methods to study in more detail the nature of these two states. We fit the temperature dependence of

the emission spectrum and obtain the energy separation of the two states. We study the temporal evolution of the emission and find very fast (<1 ns) thermal equilibrium between these two states, which is different from the surface defect states in cadmium salt NCs. We use time-resolved differential absorption spectroscopy and observe an additional fast (ps) component at low temperature, which we attribute to the formation of the polaron state. The absence of the stimulated emission peak is explained as due to the very small oscillator strength of the low energy state. Finally, the Auger recombination rate of lead salt nanocrystal is smaller at lower temperature, consistent with the picture of phonon assisted Auger recombination.

5.2 Results

5.2.1 Continuous Wave Optical Spectroscopy

Figure 5.1 shows the continuous wave (CW) absorption and photoluminescence (PL) spectra of 4.4 nm PbSe NCs, taken with a home-built spectrophotometer with a cryostat. We put the NC sample in a polyvinyl butyral polymer host (Butvar), so that they are completely isolated and do not have any electronic coupling or charge or energy transfer. It is also important that the host material should not crystalize under low temperature, thus preventing formation of crystal grain boundaries, which scatters light and makes the absolute value of absorption and PL difficult to determine. Details of sample preparation of the polymer film is described in Appendix 5.5.1. The polymer film is mounted on the cold finger of the cryostat with optical access for the measurements.

The absorption spectra of the NCs at different temperature are shown in Fig-

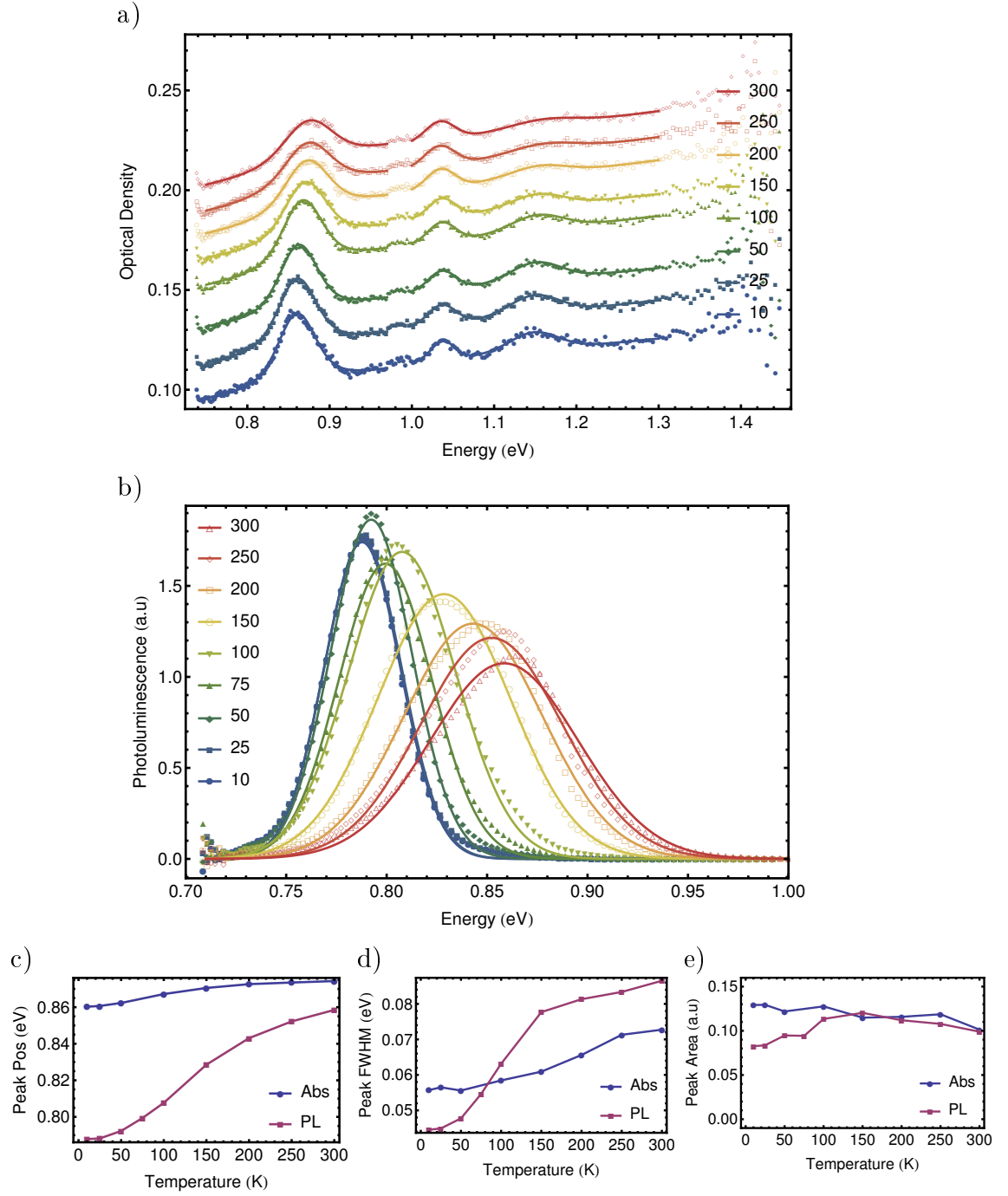


Figure 5.1: Continuous wave optical spectra. Sample: PbSe NCs embedded in polyvinyl butyral polymer. (a) Absorption spectra from 10 K - 300 K. Spectra are fitted to a Voigt function for the first peak around 0.86 eV and Gaussian functions for the two other peaks (thick solid line). (b) Photoluminescence (PL) spectra, fitted to a Gaussian function. (c) Fitted peak position, (d) full width half maximum and (e) area for the first absorption peak and PL spectra.

ure 5.1a. The first peak at around 0.86 eV corresponds to the lowest exciton transition; the second peak at around 1.04 eV, which does not change with temperature is the vibrational overtone from the polymer; the third peak at around 1.15 eV corresponds to the second exciton transition. We fit the first peak in Voigt function,¹ which treats differently the contributions from the homogeneous and inhomogeneous broadening. The second and third peaks are fitted in simpler Gaussian functions. The fitted curves are shown as the solid lines. The best fit parameters for the first peak are summarized in Figure 5.1 c,d,e. The absorption peak position shifts slowly to higher energy as temperature increases from 10 K to 300 K, with a temperature coefficient $dE_g/dT = 53 \pm 6 \mu\text{eV/K}$. Though different from normal semiconductors, it is consistent with previous study on lead salt NCs.[10] This shift was attributed to the combined effects of lattice thermal expansion, mechanical strain, electron-phonon coupling and quantum confinement. The peak width increases with temperature, due to increased electron-phonon coupling. The peak area mostly stays constant.

The PL spectra (Figure 5.1b) shows a much more pronounced shift to lower energy with decreasing temperature. We fit the spectra as single Gaussians and the parameters are compared with those of the absorption peaks (Figure 5.1c,d,e). The large red shift at low temperature is commonly attributed to the emission from a second state sitting below the first exciton state.[1, 2, 3] Indeed, the fast shift of the peak position between 100 K - 150 K is accompanied by a significant increase in the peak width, which we interpret as due to emission from two states at the same time. To analyze this further, we use a simple two-state model, which assumes that

¹The Voigt profile (named after Woldemar Voigt) is a line profile resulting from the convolution of a Gaussian profile and a Lorentzian profile: $V(x; \sigma, \gamma) = \int_{-\infty}^{\infty} G(x'; \sigma) L(x - x'; \gamma) dx'$. The full width half maximum of the Voigt profile is approximated as $f_V \approx 0.5346f_L + \sqrt{0.2166f_L^2 + f_G^2}$ where $f_L = 2\gamma$ and $f_G = 2\sigma\sqrt{2\ln(2)}$. [9]

there are two states, separated by energy ΔE , and in constant thermal equilibrium (which we will discuss in more details later), and that the relative radiative decay rate of the two states doesn't depend on temperature. According to the model, the instantaneous emission as a function of energy and temperature looks like

$$I_{PL}(E, T) = A(T) \left[r * P(\Delta E, T) * I(E; E_1(T), w_1(T)) + (1 - P(\Delta E, T)) * I(E; E_2(T), w_2(T)) \right] \quad (5.1)$$

where the lineshape function is assumed to be Gaussian: $I(E; E_0, w) = \frac{1}{\sqrt{2\pi}w} e^{-\frac{(E-E_0)^2}{2w^2}}$ (in units of Watt eV^{-4})²; the center energy and the linewidth are assumed to be linear functions of the temperature $E_i(T) = E_{i,0} + E_{i,1}T$, $w_i(T) = w_{i,0} + w_{i,1}T$; $i = 1$ corresponds to the low energy state, $i = 2$ corresponds to the high energy state; $P(\Delta E, T) = \frac{1}{1+e^{-\frac{\Delta E}{k_B T}}}$ corresponds to thermal population of the lower energy state according to the Boltzmann distribution; $1 - P(\Delta E, T)$ corresponds to the thermal population of the higher energy state; the parameter r represents the state degeneracy as well as the radiative decay rate ratio of the two states; $A(T)$ represents the temperature dependence of the overall PL quantum efficiency, and is completely free in the model fitting. This allows us to not make any assumptions about the nonradiative recombination for the states, which usually involves surface defects and are not well understood. We global fit the spectrum $I_{PL}(E, T)$ to extract the parameters.

The fitted spectra are shown in Figure 5.2a, and the spectral decomposition of the two components is shown in Figure 5.2b. As one can see, the dramatically increased emission width at around 150 K is properly fitted by the buildup of the contribution from the second peak. The best-fit energy separation of the two states $\Delta E = 30 \pm 1$ meV is close to that obtained in previous literature, albeit being extracted from different models: Gaponenko extracted $\sim 22 \pm 3$ meV splitting for

²The fit parameters changes very little if the emission is in unit of Watt eV^{-2} .

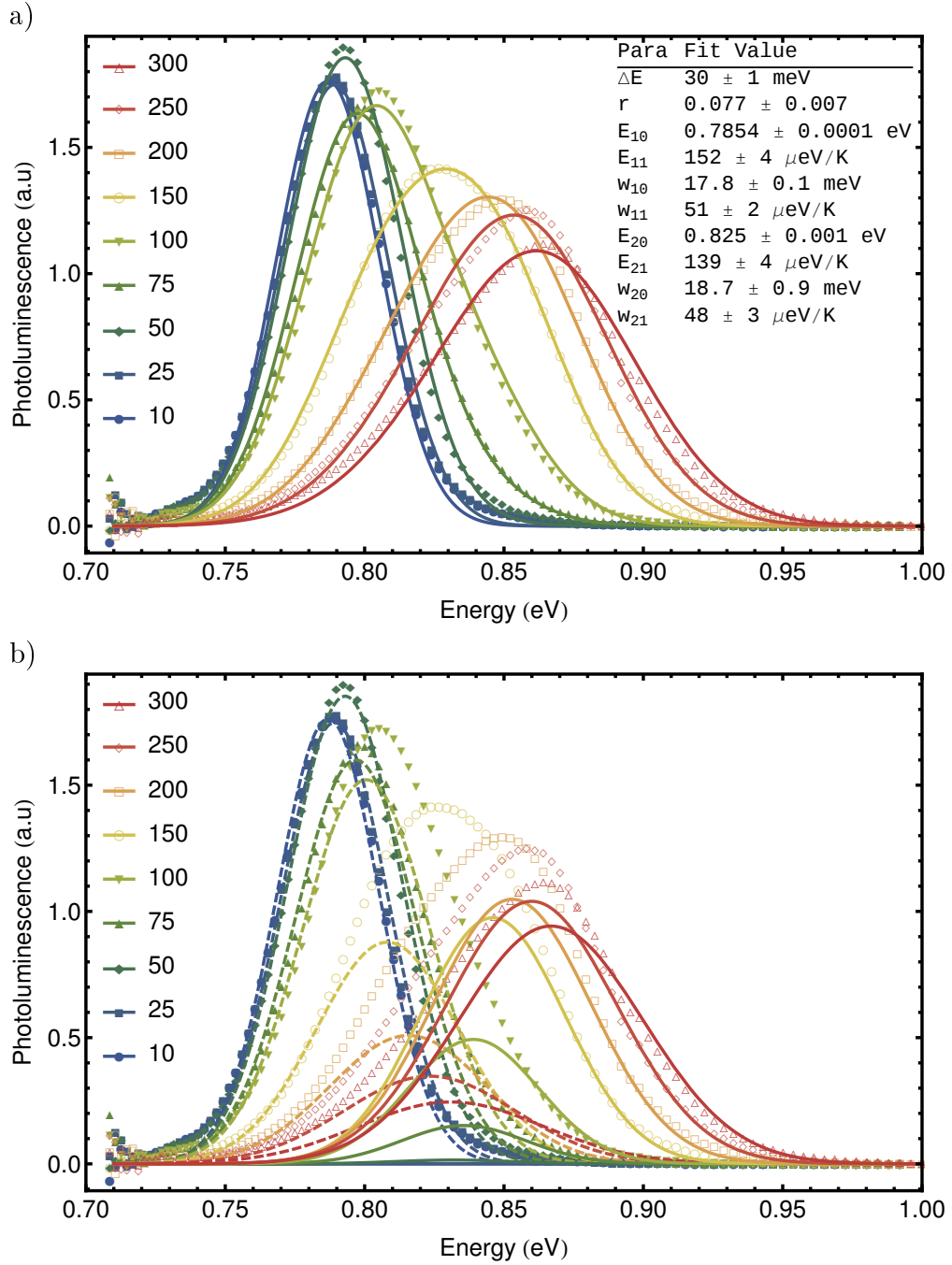


Figure 5.2: (a) Global fitting of the emission spectra, and (b) decomposition into the two components (dashed lines and solid lines) for 4.4 nm PbSe NCs embedded in Butvar, excited by 638 nm diode laser. The best fit parameters are listed in the inset.

PbS NCs, by fitting the temperature dependence of lifetime and assuming a multi-phonon nonradiative recombination model.[11] Chappell extracted 23 ± 6 meV splitting for PbSe NCs of slightly larger size, by fitting the total emission intensity to a two level system also with thermally activated trapping.[2] Admittedly, our model is crude and contains a number of assumptions about the lineshape, linear temperature dependence of energy gap, *etc.* Nevertheless, the fact that different measurements on different quantities converge to the same value for the energy splitting means that its value is robust. More intuitively, the fact that the thermal energy at room temperature (25 meV) is large enough to change considerably the relative population between these two states indicates that the energy difference is on the same magnitude. The ratio of the radiative decay rate $r = 0.077 \pm 0.007$, which means that the low energy state emits much slower than the high energy state, suggesting the possibility of the low energy state being a dark state due to fine structure splitting, or a surface state. The temperature coefficient for the emission states E_{11} and E_{21} are similar and close to $145 \mu\text{eV/K}$, but larger than the temperature coefficient for the absorption peak.

To make sure that the observation is independent of the sample preparation, we also make the same measurement on the same NCs but drop casted onto a CaF_2 window. The temperature dependence of the peak shift shows exactly the same behavior. The temperature dependence of PL intensity changes, due to change of the nonradiative recombination pathways. See Appendix 5.5.2 for more details.

5.2.2 Time-resolved Photoluminescence

To look into the state dynamics, we use time-resolved photoluminescence spectroscopy. The NCs are excited with 1 kHz, 800 nm and 130 fs pulses. We measure

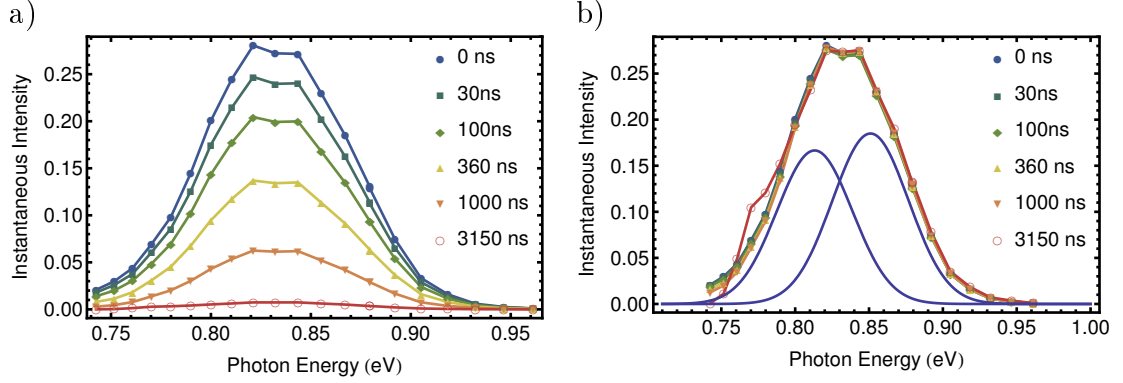


Figure 5.3: (a) Instantaneous emission spectrum at different time, for $T=150\text{K}$. (b) Normalized spectrum, to highlight the spectral overlapping. The two components extracted from the continuous wave PL data (blue solid lines) are also shown for reference.

the time traces of emission at different wavelength using an InGaAs photomultiplier tube (PMT), then stitch them together to obtain the instantaneous spectra. The instrument response of the PMT is 1 ns. Therefore, if the charge transfer happens slower than 1 ns, we'll be able to see the spectral shift.

The instantaneous emission spectra at 150K is plotted in Figure 5.3a, and the normalized spectra in Figure 5.3b. The spectral overlapping is near perfect, which shows that the thermalization between these two states is much faster than 1 ns, and the assumption we made during the fitting of the CW emission spectrum that the two states are in constant thermal equilibrium is justified. On the other hand, this is different from the surface trap state in cadmium NCs.[7, 8] There, due to the fact that the electron trapping process is an electron transfer process that is thermally activated, at low enough temperature, the transition between the core and surface state becomes slow enough that it will compete with radiative recombination.

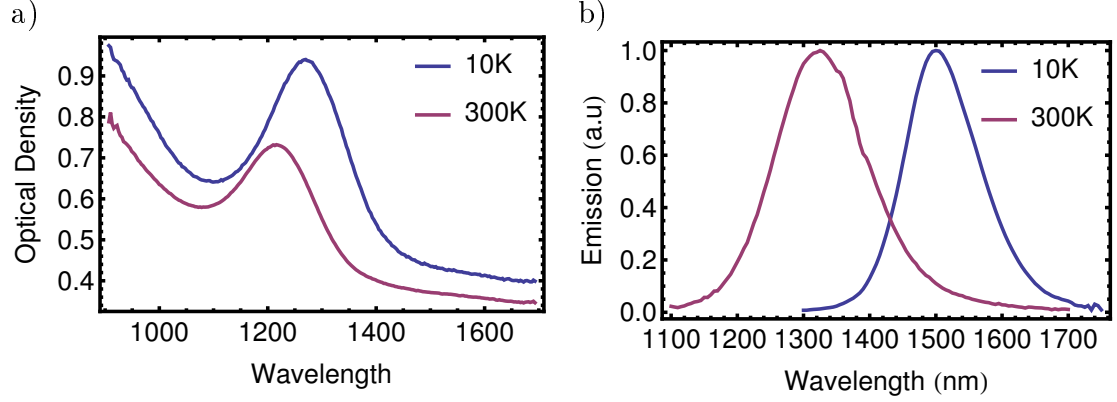


Figure 5.4: Optical characterization of 4.3 nm PbS NCs. (a) Absorption spectra at 10K and 300K. (b) Corresponding emission spectra at 10K and 300K. (c)

5.2.3 Time-resolved Differential Absorption Spectroscopy

To look further into the faster time scale, we measure transient differential absorption spectrum using pump probe spectroscopy. The pump beam is generated by an optical parametric amplifier and is set at slightly on the red side of the first absorption peak. The probe beam is a broadband ultrafast white light generated by a sapphire crystal. The generation and basic characterization of this broadband white light is shown in Appendix 5.5.3.

Due to instrument limitation, particularly the bandwidth extension of the white light on the long wavelength side, we are only able to measure differential absorption spectrum on NCs with relatively large bandgap. We choose 4.3 nm PbS NCs. Figure 5.4 shows the absorption and PL spectrum of these NCs at 10K and 300K. Clearly, the PL spectrum exhibits the same large red shift at low temperature, and we expect the state properties to be the same.

Figure 5.5 shows the results for the pump probe measurement. On the left column are measurements done at 300K, and on the right are at 10K. Figure 5.5a,b show the transient absorption traces at different wavelength. Figure 5.5c,d show

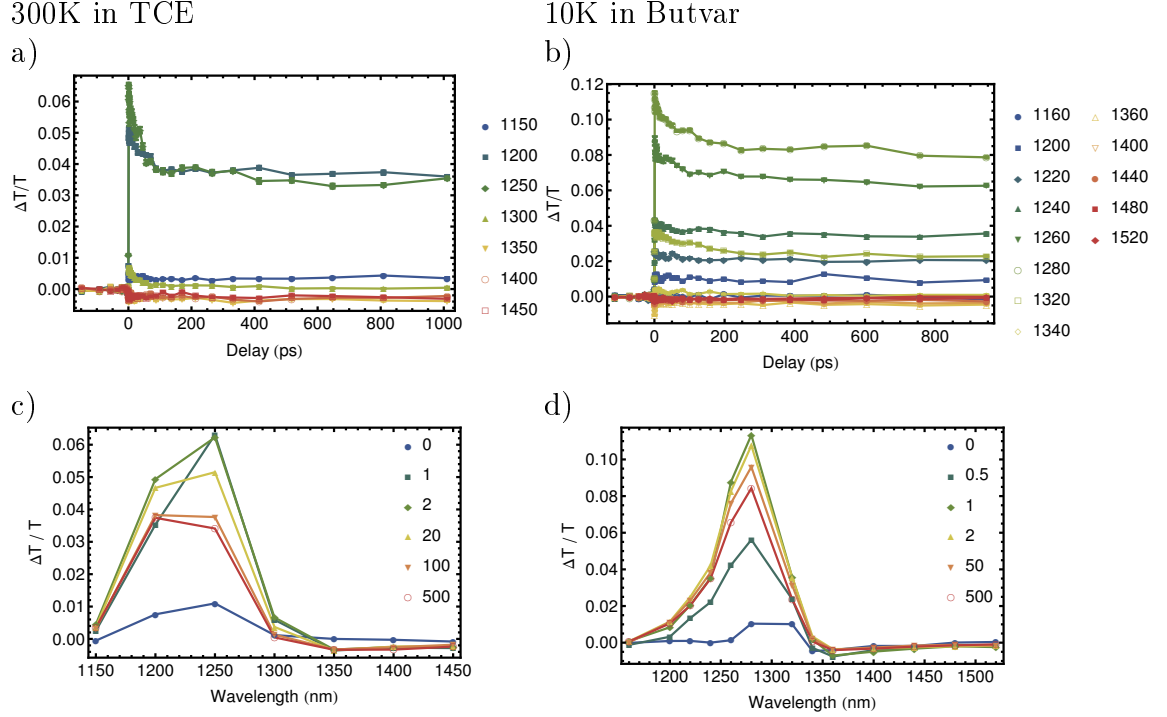
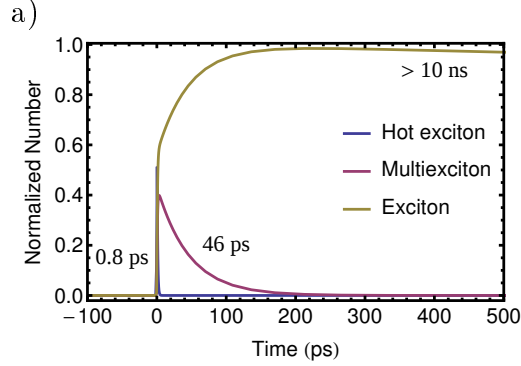


Figure 5.5: Transient differential absorption spectrum. (a) The differential absorption traces at different wavelength. Sample is 4.3 nm PbS NCs in tetrachloroethylene (TCE) at 300K. (c) Transient differential absorption spectra at different delay time between the pump and probe pulse, collected by stitching traces together. (b) and (d) are the same measurements but at 10K, on the same NCs embedded in Butvar.

the snapshot spectrum constructed by stitching the traces together. The largest feature in the differential absorption spectrum is the bleaching ($\Delta T/T > 0$) of the first exciton peak, due to state filling. The bleach peak shifts to longer wavelength at low temperature, consistent with the CW absorption measurement. The second feature is the small induced absorption at the red side of the bleaching peak, more prominent at 10 K, and is concentrated in the first few picosecond.

Using singular value decomposition, we determine that there are at least three large components in the dataset at 10K. To further isolate different components, we global-fit the time traces using a three-level cascade model ($A \rightarrow B \rightarrow C$). The model automatically separates the traces into a very short component (<1

300K in TCE



10K in Butvar

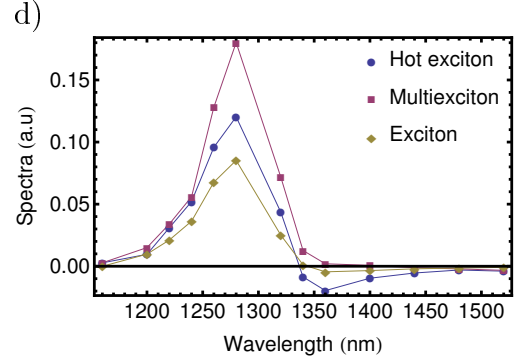
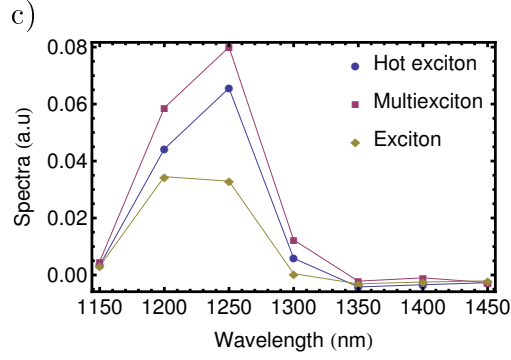
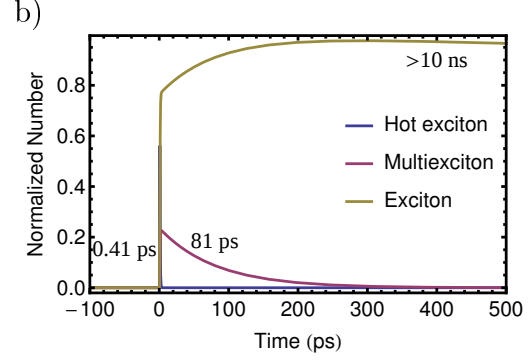


Figure 5.6: Spectral and temporal decomposition. (a,b) Temporal (c,d) spectral dependence of the three components in the 3-state cascade model, including a hot exciton state, a multiexciton state and an exciton state. (a,c) are for samples at 300K. (b,d) are for samples at 10K.

ps), which we assign as a hot exciton state, an intermediate component (~ 10 ps), the multi-exciton component, and a very long component (>10 ns), the single cooled exciton state. From the model, we extract the following picture of exciton dynamics: all the electrons are initially excited to the hot exciton state, then relax to a mixture of cooled multi-exciton and single-exciton states in subpicosecond. The multi-exciton state eventually relaxes to the single-exciton state by Auger recombination, in tens of picoseconds. The ratio of multi-exciton to single-exciton states is determined by the number of excitations per NC, which follows the Poisson distribution $P_n = \frac{\langle N \rangle^n}{n!} e^{-\langle N \rangle}$, where $\langle N \rangle$ is determined by direct calculation using the pump intensity and the absorption cross-section of a single NC. The temporal

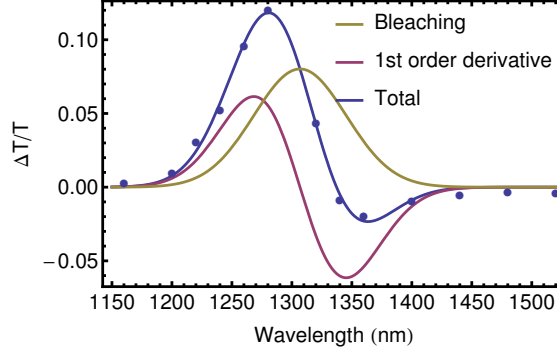


Figure 5.7: Fitting of the hot exciton spectrum (Figure 5.6d) into the difference of two Gaussian peaks (the red line minus the yellow line). The uncertainty of the fitting parameters of the two Gaussian peaks is very large, due to the differential form.

evolution of each component is shown in Figure 5.6a and b, and the spectrum for each component is shown in Figure 5.6c and d.

To make sure that the observation is independent of the sample preparation method, we did a series of control experiments, putting sample in different format, and changing the NC surface properties, and the differential absorption spectrum at 10K and 300K are all the same. This strongly suggests that the spectra that we are observing are not related to hosts material or surface defects, and are the intrinsic properties of the NCs. (See Appendix 5.5.4 for more details)

5.3 Discussion

The dip at 1350 nm for the 10 K sample is the signature of a derivative form. This has been observed previously, and was associated with the combined effect of bleaching and exciton-exciton interaction.[12, 13, 14, 15, 16] More specifically, the exciton that is created by the pump pulse creates a transient electric field, which then shifts the energy of the new exciton state, thus creating a derivative

shape in the differential absorption spectrum. We fit the “hot exciton” spectrum in Figure 5.6d as a summation of a Gaussian peak and its first order derivative and the fitting is very good (see Figure 5.7). This effect is particularly strong when the exciton is in a high energy state, in which case the bleaching signal is very small, and also higher energy exciton states have more imbalanced charge distribution thus causing larger Stark effect.[17] Appendix 5.5.5 shows the measured differential absorption spectrum when the NCs are excited by high energy photons (1.55 eV). The derivative shape is much more prominent, and its magnitude decreases as the exciton cools down to the lowest exciton state (after ~ 1 ps).

On the other hand, here we specifically excite the NCs at the red side of their first absorption peak. The exciton created by the pump pulse is already at the lowest exciton state. Therefore, the short-lived component is not that of a normal “hot” exciton. Nevertheless, it has a similar lifetime, and thus suggesting a similar energy relaxation mechanism, by electron phonon coupling. The same feature does not appear (or is very small) at 300K. (Figure 5.6c)

This transient feature is not related to the lower energy state we observed in the PL spectrum. It is short lived (~ 0.4 ps), while the lower energy state in PL spectrum is long lived (a few us). The most likely origin is still a polarization effect, but with the crystal lattice: the initial excitation creates an exciton in the lowest state. However, due to the polarization of this exciton, the lattices in the NC is not in equilibrium, and undergoes further relaxation. Essentially, it is the formation of a polaron state in a NC. The binding energy of the polaron is likely to be very small, and thus at high temperature, the exciton can populate the high energy polaron state, which explains the absence of further relaxation at 300K.

The differential absorption spectrum at 10 K after the transient process (>2

ps) is very similar to that at 300 K. The predominant component is the bleaching signal of the lowest polaron state. More importantly, there is no bleaching signal or stimulated emission peak at the emission wavelength (1500 nm). One possible explanation is that it is cancelled out by induced absorption at the same energy. However, if the stimulated emission peak does exist, it should be relatively narrow (~ 120 nm FWHM), and unless the induced absorption happens to be at the exact energy and exact width, (which is highly unlikely), these two cannot cancel each other perfectly. The more likely explanation connects back to the parameter $r = 0.077$, which we obtain from the fitting in the CW PL experiment. r represents the ratio of the state degeneracy and the radiative decay rate of the low energy peak to the high energy peak. The small $r \sim 1/13$ suggests that the oscillator strength of the low energy state is very small, which explains why the stimulated emission peak is also very small. From our signal to noise ratio in Figure 5.6d, we estimate that the low energy stimulated emission peak has to be smaller than $1/30$ of the high energy bleaching peak. Considering the eight-fold degeneracy of the lead salt bandedge, and the spin conservation in linear absorption, the bleaching peak will be five times the oscillator strength of the first excited state transition by simple state counting.³ The stimulated emission peak will be the same as the oscillator strength of the low energy state transition. This gives a total factor of $7 \times 13 \sim 90 > 30$, consistent with our observation. This, combined with a small but nonzero induced absorption to higher energy states, can completely eliminate the possibility of seeing optical gain from this low energy state.

Lastly, the multiexciton lifetime is consistently longer at low temperature compared with high temperature. Normally, Auger recombination is mediated by the Coulomb interaction between excitons. Compared with bulk semiconductor, Auger

³The absorption without the pump pulse will be $4 \times 8 = 32$ times the oscillator strength; the absorption with the pump pulse will be $4 \times 4 + 3 \times 3 = 25$, giving a difference of 7.

recombination rate in NCs is usually larger, due to the relaxation of the momentum conservation in 0D structures, thus leading to barrierless Auger recombination.[18] On the other hand, due to the atomic like discrete energy levels, efficient Auger recombination involves phonon participation.[19] Moderate increase of Auger recombination rate as temperature has been reported for CdTe NCs.[20] The same principle applies here for lead salt NCs.

5.4 Conclusion

We use a combination of continuous wave and time-resolved absorption and photoluminescence spectroscopy to study the energy levels involved in lead salt NCs. We conclude that the low energy state observed in the emission spectrum at low temperature is most likely an intrinsic state of the NC, split by exchange interaction or intervalley coupling, instead of due to surface defects or imperfect surface passivation. On the other hand, this low energy state has an order of magnitude smaller oscillator strength than the high energy state, which explains the missing stimulated emission. We also observe an additional state at low temperature, with a lifetime of about 0.4 ps. The picture is consistent with the idea of an excited polaron state. The multiexciton recombination rate increases with temperature, indicating a phonon assisted Auger process.

5.5 Appendix

5.5.1 Butvar Sample Preparation

We use polyvinyl butyral (Butvar B-76) as the polymer host. Typically 0.1 g/mL solution of Butvar in chloroform (5 mL) is mixed with NC in chloroform (30 mg/mL, 100 uL). When they are thoroughly mixed together, the mixture is poured into a glass beaker (~ 1 inch in diameter) for drying. A funnel was put on top of the beaker to make the drying process slower to avoid bubble formation. After 24 hours, the funnel is removed to speed up the remaining drying process. After 48 hours, the sample will be completely dry, and the polymer film is peeled off the bottom of the container. The whole process is done in the glovebox to avoid air exposure to the NCs.

5.5.2 PL Spectrum of Dropcasted NC Film

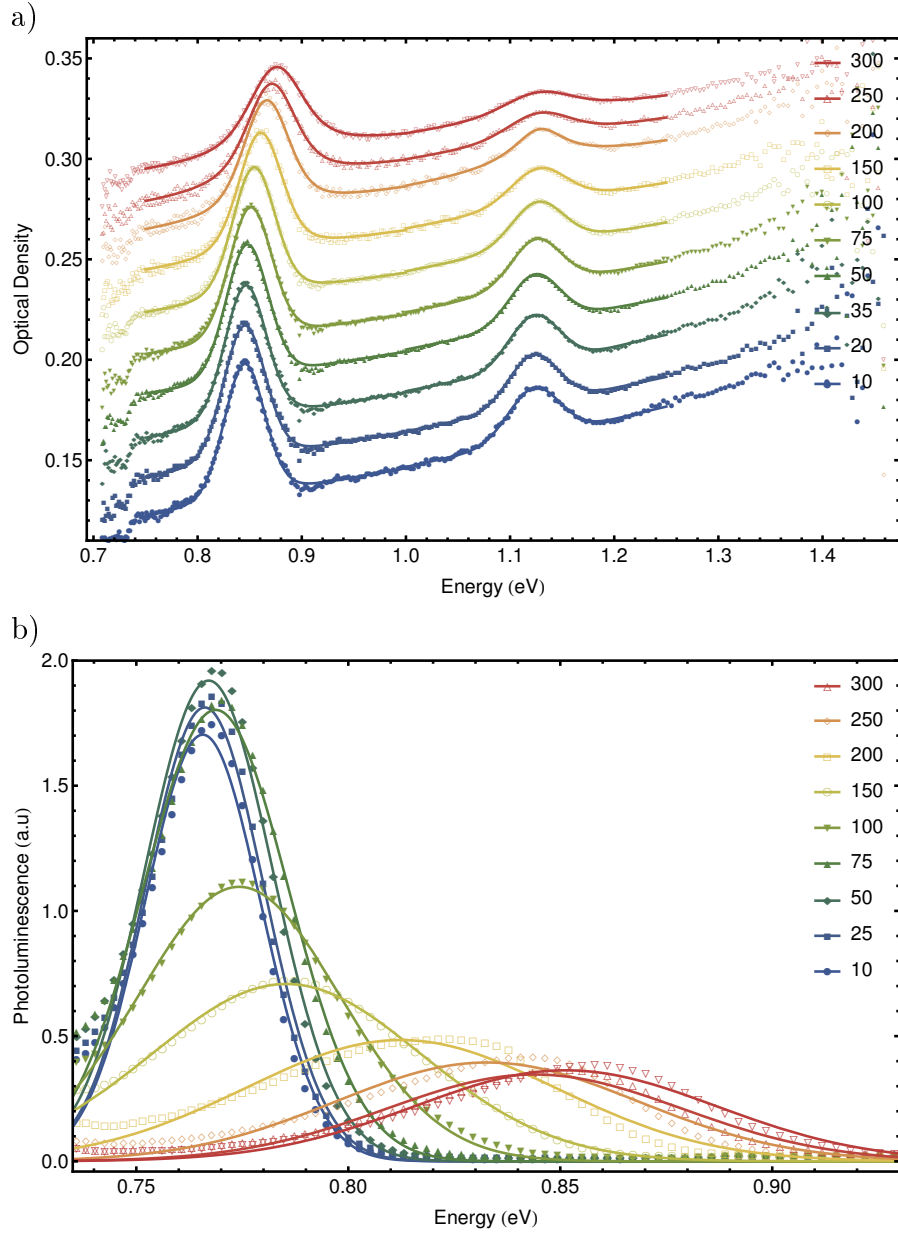


Figure 5.8: Absorption (a) and photoluminescence (b) of dropcasted 4.4 nm PbSe NCs.

Figure 5.8 shows the CW absorption and PL spectrum of dropcasted 4.4 nm PbSe NCs. Compared with Figure 5.1, the overtone absorption peak of the polymer is gone. The first and second peak position of the NC are almost exactly the

same. The emission intensity significantly drops at higher temperature, due to the activation of extra recombination pathway at higher temperature.

5.5.3 Broadband White Light Generation

In order to excite the NCs at the first absorption peak, while still having the capability of measuring absorption at a large wavelength range, we choose to use a broadband white light generated by high order nonlinear effects in a nonlinear crystal as the probe. Sapphire crystal is used mainly for two reasons: (1) it has negligible absorption in the near infrared region; (2) it has a very high thermal damage threshold. The generation setup is like this: a 1 kHz, 800 nm, 130 fs pulse train from the regenerative amplifier is used for the excitation source. Energy per pulse is <200 uJ, and is further modulated by a linear polarizer and a half wave plate as a variable attenuator. The beam is focused by a 150 mm focusing lens onto a 100 μ m circular pinhole mounted on a two-axis translation stage for spatial filtering, before it is refocused by a 30 mm lens onto a 5 mm sapphire crystal, which sits on a three-axis translation stage for fine position tuning. After filtering out the residual 800 nm light, the white light is refocused using an achromatic lens onto the sample where it is overlapped with the pump beam. After the sample, the white light is recollimated and send to a monochromator and photodiode for measurement.

Due to the fact that it's a very high order nonlinear process, even after the pulse spatial filtering, due to the inherent pulse energy and direction fluctuation, as well as air turbulence, the white light generated shows spatial flickering, and energy fluctuation on 100 ms time scale. To further improve signal to noise ratio, we integrate the light intensity readout in two separate channels. The pump beam is

modulated with a synchronized chopper so that every other pump pulse is blocked to provide a reference. One channel collects all probe signals and averages them on a 100 ms time scale, to provide T ; the other channel collects all probe signals but with alternative parity, thus providing ΔT . It is then divided by the output of the first channel, and then averaged to provide $\Delta T/T$. Using this method, we can measure $\Delta T/T \sim 5 * 10^{-4}$ with 1 s average time from 1200 nm to 1400 nm.

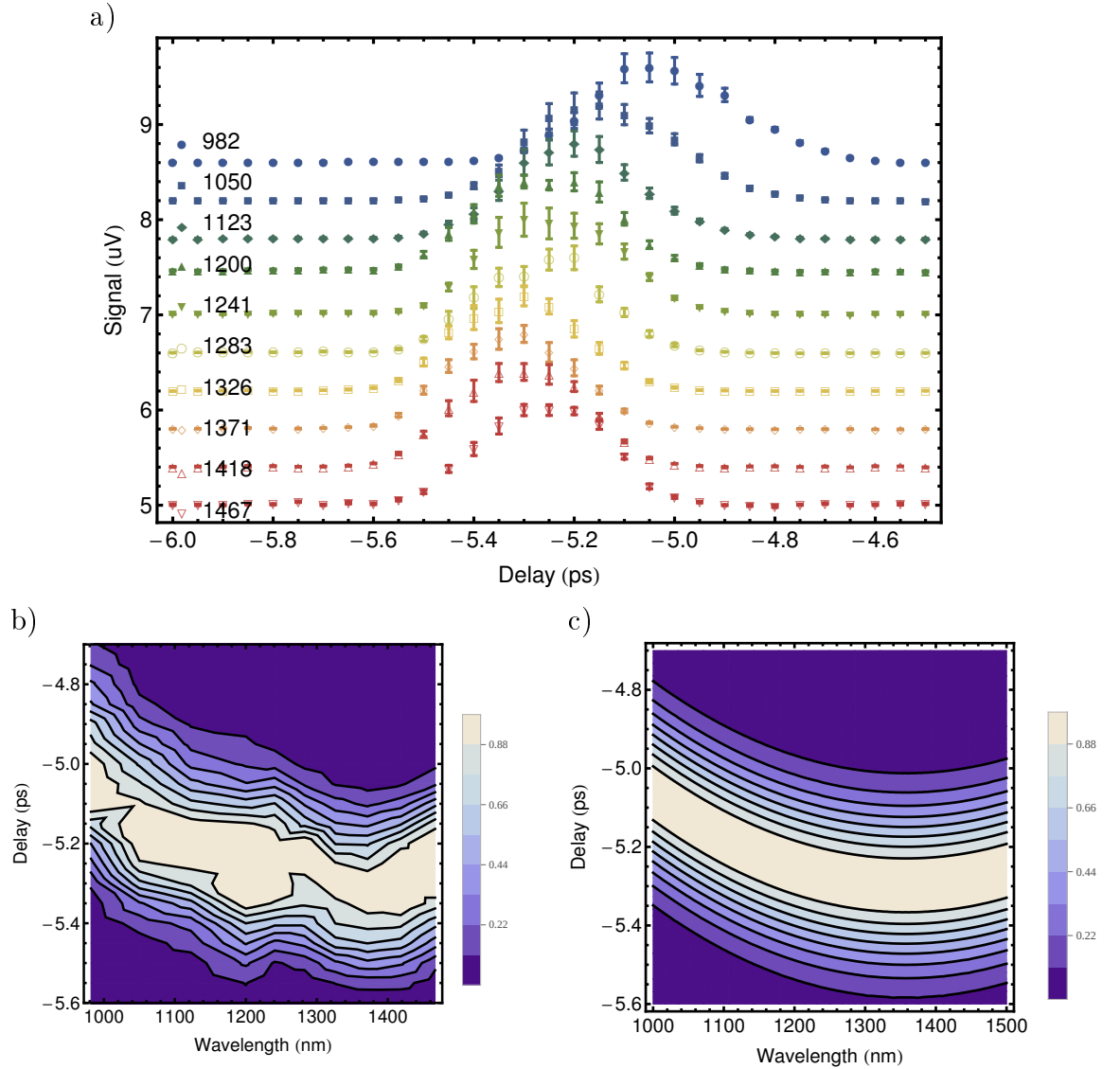


Figure 5.9: Ultrafast broadband white light generation characterization. (a) Cross correlation of white light with 1200 nm light. (b) Contour plot of the intensity. (c) Fitted intensity, assuming a parabolic group delay dispersion.

Figure 5.9 shows the cross correlation of the generated white light with a 1200 nm reference beam. There is a small chirping of the output pulse. It was fitted a simple parabolic model and is used to correct the collected data. The FWHM of the cross correlation is 320 fs, which is our temporal resolution.

5.5.4 Transient Absorption on Samples with Different Hosts and Surface Modification

To make sure that the spectrum is independent of the sample preparation method, we did a series of control experiments, putting the sample in different format, and changing the NC surface properties.

Figure 5.10 shows the transient differential absorption spectra for different samples. They all use the same NCs. Figure 5.10a has NCs spin coated onto a glass slide, and measured at 300K. Compared with the results in Figure 5.5a, it shows the same dominant bleaching signal at the absorption peak position. There is a very small amount of induced absorption at the longer wavelength (>1330 nm), persists over long time. Figure 5.10b shows the same sample but at 10K. Again, there is a more prominent short lived component of induced absorption at long wavelength. Figure 5.10c shows the result with NCs treated moderately with tetrabutylammonium iodide (TBAI). Previous studies show that these atomic halide can increase surface passivation and air stability of NCs.[21, 22, 23] Figure 5.10d shows the result with NCs that has two extra washing cycles with a mixture of ethanol and methanol. Previous studies show that extra washing progressively removes surface passivating ligand, which creates surface defects.[24] Again, both show almost identical results compared with 5.5d, indicating that the spectra that we are ob-

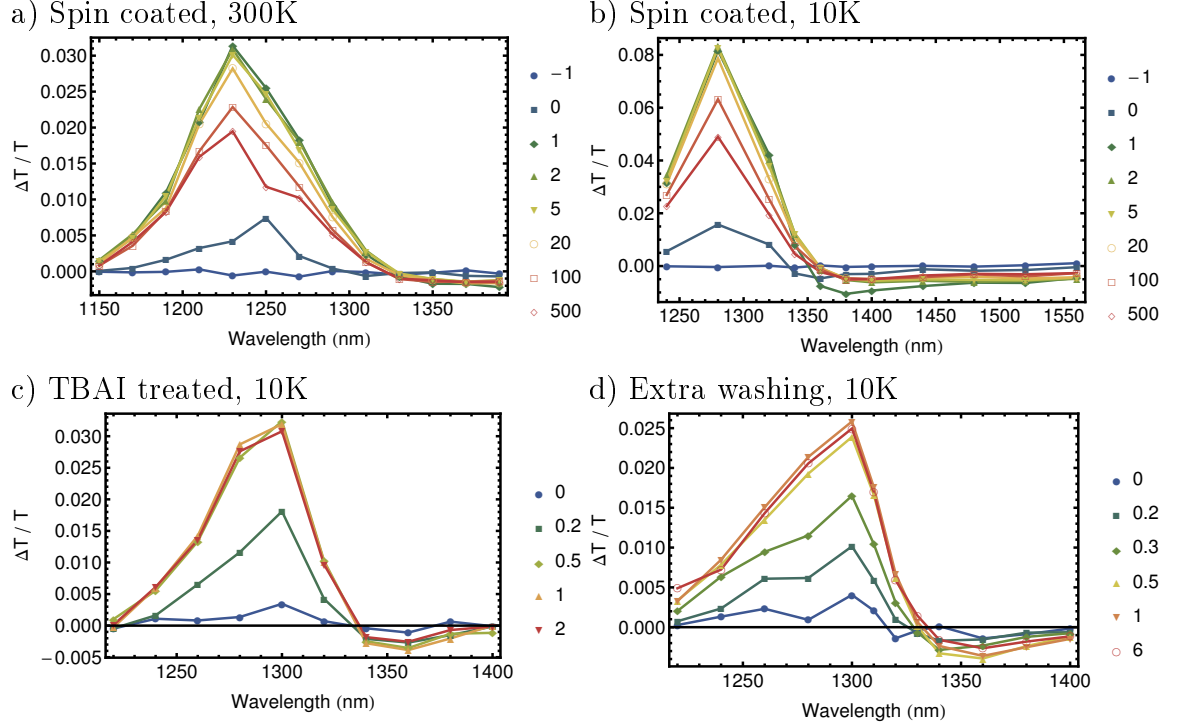


Figure 5.10: Transient differential absorption spectra for samples with different hosts and surface treatment. (a) NCs spin coated onto glass slide, one layer, no ligand treatment, measured at 300 K, excited at 1250 nm. (b) Same sample, measured at 10 K, excited at 1300 nm. (c) NCs treated with tetrabutylammonium iodide (TBAI) and embedded in Butvar, measured at 10K, excited at 1300 nm. (d) NCs washed with a mixture of ethanol and methanol twice more and embedded in Butvar, measured at 10K, excited at 1300 nm.

serving are not related to surface defects, and are the intrinsic properties of the NCs.

5.5.5 Transient Absorption Pumped at 800 nm

Figure 5.11 shows transient differential absorption spectrum when NCs are excited by high energy photons (1.55 eV), thus generating a real hot exciton. Here the exciton exciton interaction is a lot stronger, and the bleaching signal is absent, until the exciton relaxes to the lowest energy state.

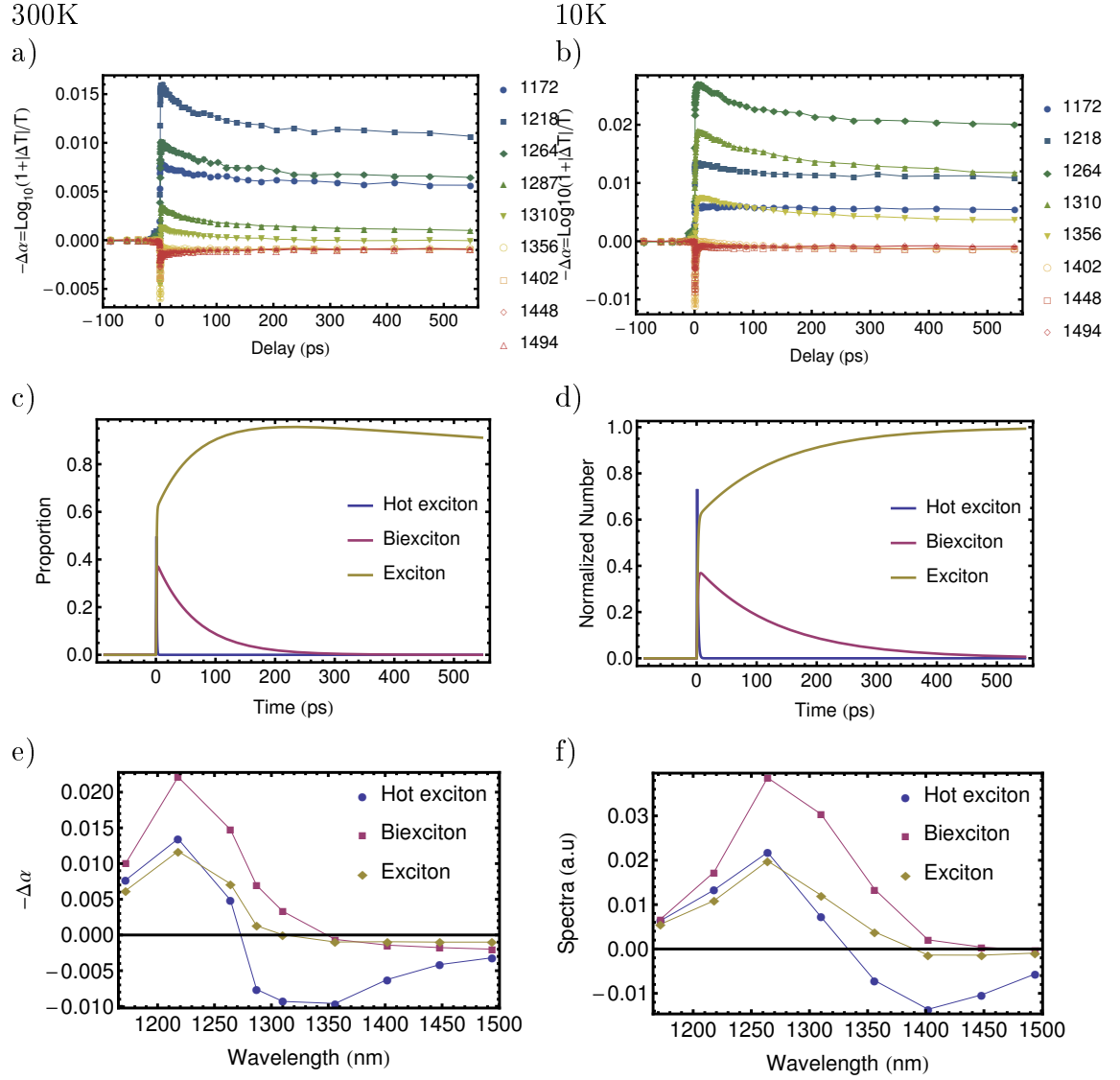


Figure 5.11: Transient differential absorption spectrum for NCs excited by a high energy photon (1.55 eV). The hot exciton generated induces a large red shift in the energy of the ground exciton, thus creating a large differential spectrum. This happens at both high and low temperature. Sample: PbS NC 4.3nm embedded in Butvar.

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CHAPTER 6

FUTURE DIRECTIONS

6.1 Alternative Transport Measurement

With recent fast development on strongly coupled NC solids as well as different NC superlattices with atomic precision, there is an ever more urgent need for precise characterization of their transport properties. In normal cases, transport is measured using a field effect transistor (FET). On the other hand, due to the method of making these nanostructures using self-assembly, typically these nanostructures have grains on the order of 100 nm to a few micrometers. Directly measuring transport in a single grain, which is extremely important in understanding the fundamental charge transportation in these metamaterials, requires an FET with a conducting channel of hundreds of nanometers in width. Such small size generally requires the use of e-beam lithography, which is expensive and time consuming. Alternatively, atomic force microscopy and related electric force microscopy and kelvin probe microscopy could be very useful in probing these local properties. In fact, kelvin probe microscopy has already been used extensively in studying charge transportation in 1D and 2D materials, such as epitaxially grown semiconductor,[1] carbon nanotube,[2, 3] graphene,[4] polymer,[5], and also in diagnosis of optoelectronic device operations.[6] Only recently, the method is starting to be used on studying transport in semiconductor nanocrystal solids.[7]

Figure 6.1 shows the result of early measurement we did on NC solids treated with short ethanedithiol (EDT) ligand. The short ligand replaces the original long ligand on the NC surface, bringing NCs closer to each other, and improving the charge transport efficiency. On the other hand, due to the volume contraction,

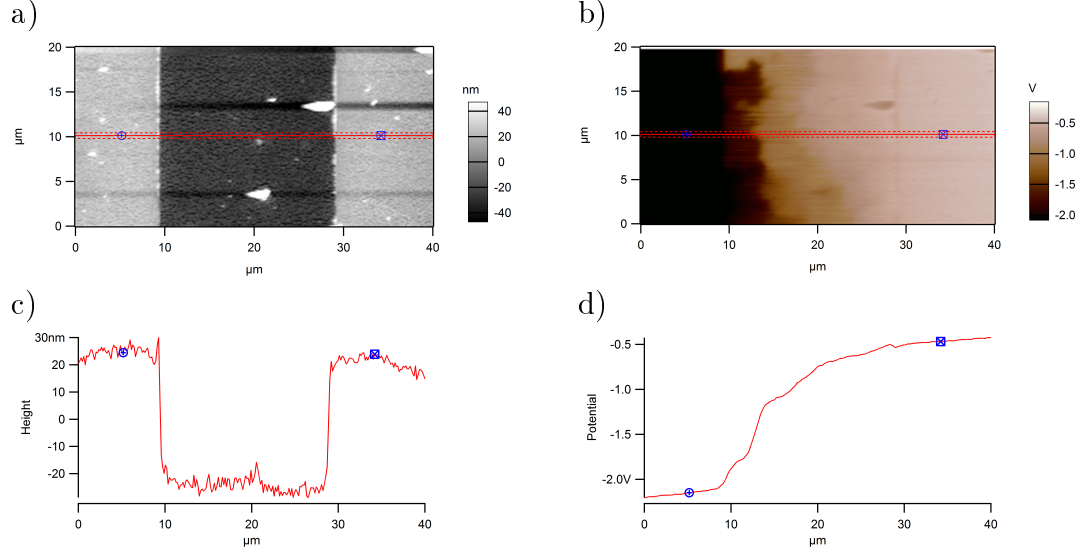


Figure 6.1: Morphology (a) and surface potential (b) mapping on ethanedithiol linked nanocrystal solids. Image (c) and (d) are the corresponding cross-section plot.

there is usually grain boundaries emerging in the solid. We deposited one layer of about 10 nm thick NC film on a 20 μm channel. The grain boundaries were very narrow (a few to tens of nanometers) and didn't show up in the morphology measurement (Figure 6.1a). However, when we biased the channel (2V), and measured the surface potential, there existed these discrete jumps, which corresponded to the grain boundaries with significantly larger resistance (Figure 6.1b) compared with in-grain transport. Careful measurement of the ratio of the in-grain resistance *vs.* across grain resistance can tell us how much does transport through these grain boundaries affects the overall transport efficiency. The conducting channel can be gated to change the Fermi level of the NCs, just like in ordinary FET measurements.

The major difficulty of these measurements is the proper sample handling. It was found that NC surface is so sensitive that just seconds of exposure to the ambient environment will greatly affect their transport properties. Typical

transistor measurements are all done in the inert environment, such as a glove box. It is difficult to put an entire AFM in a glovebox, and one cannot use an inert cover material to protect the NCs, which would block the access for the AFM probe. Nevertheless, there are ways to get around these limitations. For example, the Asylum MFP 3D-Bio-AFM in the Cornell Center for Material Research center, has a special holder than can seal the sample with the AFM probe in an inert environment before assembled on the AFM head for measurement, thus eliminating any exposure to the ambient environment. The other possibility is to use a cover that can be opened in vacuum, and use the AFM in vacuum. The added benefit of this is that in vacuum the probe sensitivity is usually a lot higher.

6.2 Alternative Superlattice Structure

For efficient optoelectronic devices based on NCs, we need good transport properties while maintaining the quantum confinement. The standard strategy is to make NCs with strong quantum confinement, and then move them closer and closer together for stronger electronic coupling. The opposite way of doing this is to make a good transport material, such as a bulk semiconductor (bulk lead sulfide has electron and hole mobility of $600 \text{ cm}^2/\text{Vs}$) and then reintroduce quantum confinement, such as an inverse opal (see Figure 6.2).[8] A lot of the early works on inverse opal structures were focused on using the periodic structure as a photonic crystal for light trapping,[9] or using the large surface area for charge separation.[10] Recently, the focus is shifting to their electronic properties. For example, Lin and his coworkers has reported inverse opal for CdS with good electrical conductivity.[11]

Typical strategies to make these inverse opal structures involve using a tem-

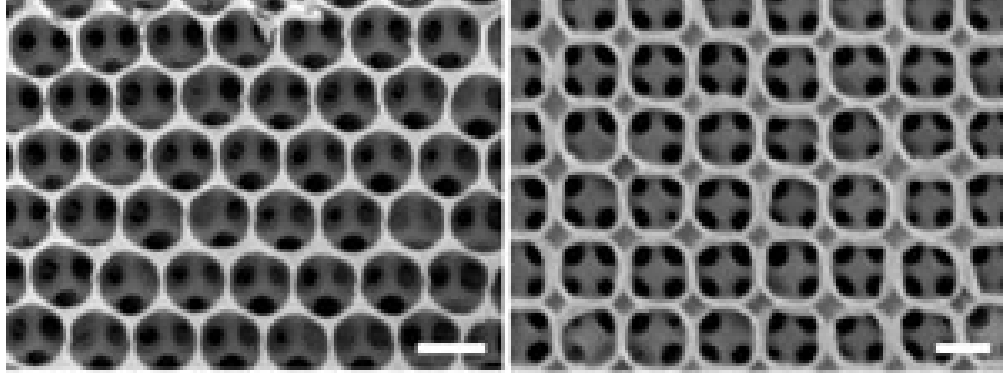


Figure 6.2: Titania inverse opal photonic crystals. Views along the 111 (left) and 100 (right) face-centered cubic crystal axes. Scale bars are 300 nm. (Courtesy of Bartl Group, the University of Utah)

plate, such as self-assembled polystyrene spheres.[8, 9] The inverse opal material is then filled in or grown in the interstitial volume. Afterwards, the template is removed, usually by calcination. The desired material can also be introduced in terms of coassembly with the template,[11] and thermal annealing afterwards to help improve crystallinity.

Lead salt semiconductor is an ideal material for inverse opal structures to study their electronic properties. First, their Bohr radius is very large, owing to the small effective mass and large dielectric constant. As a result, it is easier to make lead salt nanostructures of moderate sizes that have strong quantum confinement. Second, lead salt, especially lead selenide has a surface layer that is very mobile. This is one of the reasons why 1D and 2D lead salt nanostructures can be made from orientated attachment of small NCs, and why post-synthesis morphology change is possible. This can greatly facilitate crystallinity of the inverse opal after the assembly. Third, one of the problems with inverse opals is their structural integrity after the template is removed. However, for lead salt, this step maybe not be necessary, or even desired. Their small bandgap means that a lot of materials will simply serve as the energy barrier for the quantum confinement. One can also

envision potential structures similar to bulk heterojunction where electrons and holes transport in separate materials for efficient charge extraction and collection.

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