

Simulation of Quantum Dots

Group project

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Abstract

In this group project, we made ourselves acquainted with the subject of quantum dots (QD) and QD solar cells as an application thereof.

We used OMEN, a simulation tool for nanoelectronic devices, to simulate lead sulfide (PbS) QDs and created a MATLAB toolbox which simplifies the simulation as well as the management and visualisation of simulation data significantly.

Furthermore we simulated the eigenenergies and eigenstates of PbS QDs for different parameters and analyzed the data. In particular, dependencies on the QD's size and on the electric field were investigated. In the case of band gaps, we compared the results with experimental absorption data.

During the project, we also had the possibility to observe nanocrystal synthesis in the laboratory.

Chapter 1

The Quantum Dot

Quantum Dots (QDs) are atomic structures (usually spherical) that have a size of about 1-10nm in diameter. They are often referred to as nanocrystals (NCs), though this term is more general and includes also other shapes and morphologies, which might extend to several μm , such as rods, wires etc. Figure 1.1 gives some examples of possible shapes and morphologies, that are possible with nowadays technologies.

QDs of various materials such as metals, semiconductors and compounds exist. According to their size and material, a QD can contain just a few or millions of atoms. A 10nm cube of GaAs contains for example 40,000 atoms [2].

The properties of QDs are strongly dependent on their size. Figure 1.3 illustrates this effect for a semiconductor QD. Under ultraviolet excitation, the QDs emit light according to their size and therefore band gap.

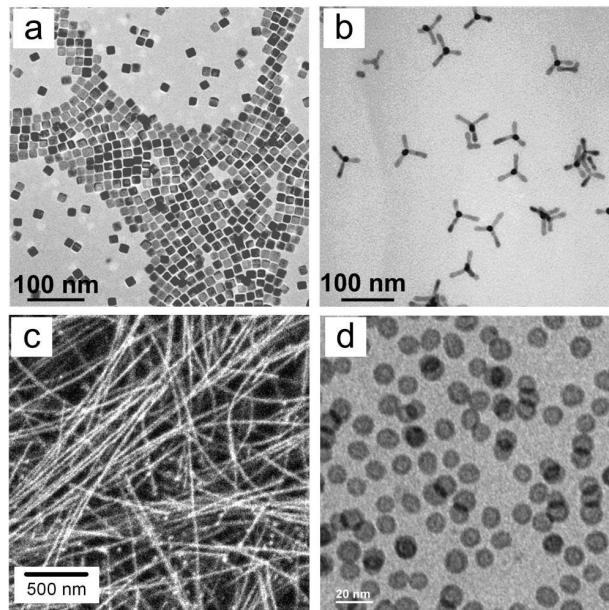


Figure 1.1: Examples of inorganic nanomaterials with different shapes and morphologies synthesized by colloidal chemistry: (a) PbSe cubes; (b) CdTe tetrapods; (c) PbSe nanowires and (d) hollow iron oxide nanoparticles. SOURCE: [5, p.394]

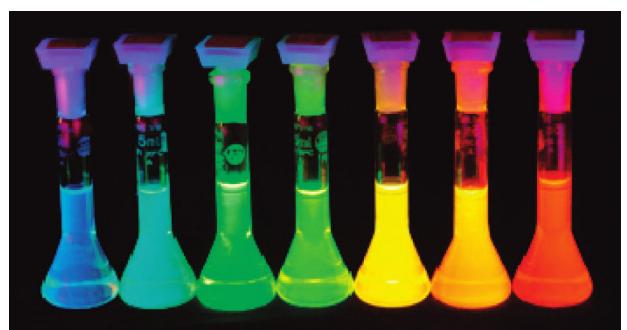


Figure 1.2: This photograph shows the size-dependent PL of the QDs. The particles with the smallest ($\sim 1.7\text{nm}$) CdSe cores emit blue and those with the largest cores ($\sim 5\text{nm}$) emit red. SOURCE: [5, p.393]

Basic physics of the QDs For bulk materials the band gap is a fixed material parameter. But when a particle gets smaller and reaches a size of about 10nm, this will not be the case anymore. The band gap is then depending on the size of this particle (NC). As the mobility of the charge carriers (electrons, holes) is very limited in all three dimensions in the quantum dot, the energy levels are not continuous, but instead discrete. This phenomenon is called the *quantum size effect*.

The band gap of a spherical QD of radius R is then approximately:

$$E_g \approx E_{g,0} + \frac{\hbar^2 \pi^2}{2m_{eh} R^2} \quad (1.1)$$

where $E_{g,0}$ denotes the band gap of the bulk material and m_{eh} is the reduced mass of the effective electron and hole masses $m_{e,p}$:

$$m_{eh} = \frac{m_e m_h}{m_e + m_h} \quad (1.2)$$

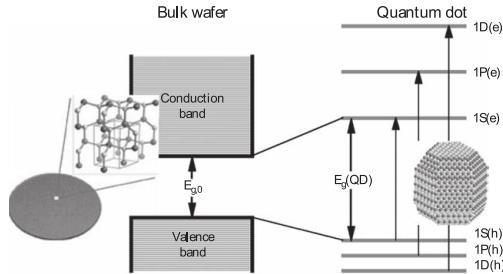


Figure 1.3: The left illustration shows the band structure of a bulk semiconductor with energy band gap $E_{g,0}$, whereas the the right one illustrates the discrete energy levels of a QD and its energy gap $E_g(QD)$. SOURCE: [11, p.3]

We will see in chapter 5.2 that the QD absorption spectrum, as shown in figure 1.3(c), is not really discrete. Since it is not possible to fabricate QDs that are perfectly equal in size, this results in a broadening of the spectrum. The energy gap increases for decreasing QD sizes, because more energy is required to confine the electron to a smaller volume. This is caused by Heisenberg's uncertainty principle , which states, that if we want to locate a particle of effective mass m (for example an electron), within an interval Δx , we can only make an uncertain prediction of its impulse. If the spatial region gets smaller, the uncertainty of the impulse will increase.

$$\Delta p_x \sim \frac{\hbar}{\Delta x} \quad (1.3)$$

This adds to the kinetic energy of the free particle, which is called the confinement energy. It has an significant impact, if it gets bigger than the thermal energy of the particle.

$$E_{confinement} = \frac{(\Delta p_x)^2}{2m} \sim \frac{\hbar^2}{2m(\Delta x)^2} > \frac{1}{2}k_B T \quad (1.4)$$

From this we can conclude, that the quantum size effect is relevant if

$$\Delta x < \sqrt{\frac{\hbar^2}{mk_B T}} \quad (1.5)$$

Table 1.1 shows four possible confinement structures, which are illustrated in Figure 1.4 with their characteristic energy levels in the conduction band.

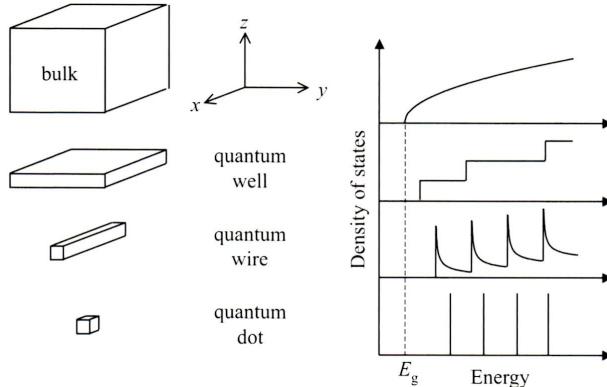


Figure 1.4: Schematic representation of quantum wells, wires and dots (left). The generic shape of the density of states function for electrons in the conduction band of a semiconductor with band gap E_g is shown for each type of the structure (right). SOURCE: [7, p.143]

Structure	Quantum confinement	# of free dimensions	Electron density of states
Bulk	none	3	$\propto E^{1/2}$
Quantum well/superlattice	1-D	2	$\propto E^0$
Quantum wire	2-D	1	$\propto E^{-1/2}$
Quantum dot/box	3-D	0	discrete

Table 1.1: Number of degrees of freedom tabulated against the dimensionality of the quantum confinement. The final column shows the functional form of the density of states for free electrons. SOURCE: [7, p.142]

Fabrication techniques of QD A lot of different ways to make QDs have been developed. Research efforts are made to create more efficient QDs, new shapes and morphologies. As QDs are more and more interesting for various commercial applications, low costs are an important factor. The colloidal chemistry has made a major contribution, as it offers low energy synthesis of NCs/QDs using very simple and affordable laboratory equipment. In the next chapter we will briefly discuss the mentioned technique, by giving a short overview while avoiding the use of chemical terms as much as possible, rather than providing a detailed disquisition, as this is a research field on its own.

Some methods are listed below.

Physical methods

Molecular-beam-epitaxy (MBE)
Metalorganic-chemical-vapor-decomposition (MOCVD)
Vapor-liquid-solid (VLS)
Electron-beam lithography

Characterization

High-energy-input, expensive apparatus, used for QDs
High-energy-input, used for QDs
High-energy-input, used for quantum wires

Chemical methods

Colloidal chemical synthesis of crystalline semiconductor nanoparticles

Characterization

Low-energy-input, wet chemistry, used for various structures

Applications In biology and chemistry QDs are used as spectral tags that are attached to molecules, making their position visible for identification under optical illumination. In the past, one used organic dyes, but compared to QDs the sharpness of the emission lines is not as good.

In electronics, QDs are used to increase the efficiency of lasers [16], everyday light sources and solar cells. Furthermore they are used in broadband light-emitting diode (LED), memory elements, flexible displays and photodetectors.

We have to add that a lot of these applications are still developed in research institutions and are not yet available for commercial use.

Although the applications seem impressive and will probably motivate new technologies, there are reasonable concerns about these nanoscale particles. Some of the materials are toxic and through the small sizes it is unclear what might happen if the particles end up in living organisms or generally speaking, in the environment. For more interested readers, we recommend the following paper for further reading: Hardman “A Toxicologic Review of Quantum Dots: Toxicity Depends on Physicochemical and Environmental Factors” [8].

Chapter 2

Colloidal Nanocrystal Synthesis

The colloidal chemistry has offered a remarkable amount of tools for creating nanostructures. In the past, growing simple, spherical, monodisperse NCs was the starting point of this research area, whereas nowadays various shapes, such as spheres, cubes, tetrapods, wires or rods can be engineered. The main advantages of the colloidal synthesis are:

- High precision shape control of the crystal and multicomponent structures
- Good size adjustability, through which the optical properties of the material are determined
- Monodispersity of the NC
- Low energy and low cost fabrication with a simple experimental setup
- Broad range of materials, including metals, semiconductors and magnetic materials can be synthesized at sub-20nm range

Due to the listed advantages, the colloidal NC synthesis is the best candidate for commercial applications so far.

Remark. In the following section, we will use some chemical terms. Their meaning can be looked up in the glossary on page 37.

2.1 The Synthesis

The colloidal NC synthesis is a wet chemical method to create nanostructures. It is based on a three-component system composed of precursors, organic surfactants and solvents. Its basic idea is the controlled growth of a NC, which is mainly depending on time.

The basic apparatus of the synthesis is given in figure 2.1. It shows a reaction flask with thermometer and injection in form of a syringe. In praxis, a heater is installed around the lower part of the flask, to keep the solvent at a desired constant temperature. The procedure itself starts with the heating of a solvent funneled into the flask. The thermometer will indicate the temperature of the solvent, which is a key variable for a good growth process. Therefore, temperature is important to control, especially since the reaction will have an influence on the temperature as well.

Figure 2.1 furthermore illustrates the stages of the synthesis using the traditional LaMer model by the U.S.-American chemist Victor LaMer. The nucleation process starts after the injection of the precursors into the flask, where they decompose and form monomers, which will cause the nucleation and growth of the NCs. The size of the NC is at this stage primarily determined by the time, i.e. the longer the reaction, the larger the crystals will grow. The energy required to decompose the precursors is provided by the solvent in the flask, either by thermal collisions or by a chemical reaction between the liquid medium and the precursors or by a combination of these two mechanisms [15]. Once monomer concentrations are sufficiently depleted, growth can proceed by Oswald ripening. Smaller particles combine with larger ones and cause therefore a lower concentration of particles in the solution. Unfortunately, the process is more complicated, as the model predicts. It does not hold for hot-injection schemes for instance, because nucleation, ripening and growth may almost occur concurrently [11, p.5]. Furthermore the nucleation process does not have to start immediately after injection, but it is usually a single discrete event in time. In the following paragraph we will explain the variables that influence the reaction and their relationship to each other.

As soon as the final size is reached, the reaction is stopped, by switching off the heating and cooling down the compound. After the reaction is stopped, the NCs are washed to remove impurities from the reaction.

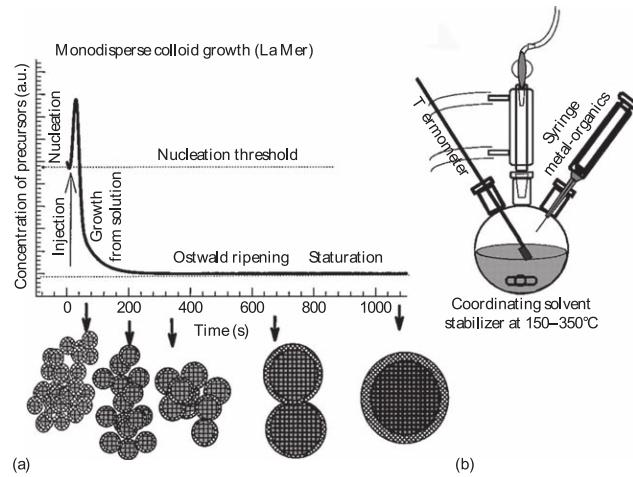


Figure 2.1: (a) Stages of the monodisperse NC synthesis according to La Mer. (b) Basic apparatus used in the synthesis. SOURCE: [11, p.4]

2.2 Reaction Conditions

Typically, finding the right conditions for a reaction is a very difficult task. For different materials, the conditions change and the reaction components have to be tailored exactly for this specific material. Hence finding an optimal set of conditions decides over the quality of the resulting NCs.

Duration of the particle growth As mentioned, the duration of the process after injecting the precursors, determines the size of the particles. One might ask, when the right moment has arrived to stop the synthesis, because the particles itself cannot be measured during the reaction. Due to this fact, the time to reach a desired size is determined empirically.

Reaction temperature The temperature is a critical factor for determining optimal crystal growth. High reaction temperatures of 125°C-400°C are often needed to anneal out defects in the crystalline lattice to form highly crystalline particles [15]. In addition to that, precursors have to withstand such high temperatures on the one hand and on the other hand temperatures need to be high enough, that precursors turn into monomers. This contradiction makes researchers to look for specific materials that fit the needed conditions.

Concentration of surfactants The choice of surfactants varies from case to case: a molecule that binds too strongly to the surface of the QD is not suitable, as it would not allow the crystal to grow. On the other hand, a weakly coordinating molecule would yield large particles or aggregates.

The combination of these conditions decides, if the final QD is of poor or high quality. Especially for semiconductor QDs a high luminescence efficiency is of great importance, since one would like to use the NCs for example in solar cells. Therefore a high efficiency rate would increase the performance of the photovoltaic elements. This can be achieved by a proper control of surface chemistry, as this can eliminate midgap states associated with surface dangling bonds [5].

Chapter 3

QD Solar Cells

This chapter gives a brief overview over the fundamental principles of photovoltaic cells and QD solar cells in particular, then focusing on the example of PbS cells to give some specific information.

3.1 Solar Cell Principles

The basic idea of a solar cell is to convert light into electrical power. Light is absorbed in a material, thus generating an electron-hole pair. The generated electrons and holes must then be separated and conducted to electrodes attached to the material. The accumulation of carriers at the electrodes generates a potential difference, and a current will flow between the electrodes, if a load is connected.

The carrier separation can be achieved by an electric field inside the material. Different types of solar cells exist based on different approaches. The typical silicon solar cell uses a semiconductor p-n junction: When a photon (with energy greater than the band gap) is absorbed in the semiconductor, an electron is promoted from the valence to the conduction band. Near the junction, these photogenerated electrons and holes are swept away to different sides, due to the built-in electric field of the p-n junction (figure 3.1).

Other approaches are also widely used, for example Schottky contacts (metal-semiconductor interface) or semiconductor-liquid interfaces.

The electrical behaviour of a photovoltaic cell can be well described by its I-V characteristics (figure 3.2). In the dark, the cell behaves like a diode (in the case of a p-n junction solar cell this seems fairly obvious). Under illumination, the curve is shifted vertically downwards. It crosses now the fourth quadrant, where the electrical power $P = IV$ is negative, which indicates that power is delivered to the load.

To characterise the solar cell, there are some common parameters, which are mentioned in the following paragraph. The open-circuit voltage V_{OC} is the maximum voltage provided by the cell. It is directly related to the energy band structure and thus to the built-in potential. The short-circuit current I_{SC} gives the maximum current, which flows if the electrodes are connected. I_{SC} is proportional to the carrier density under illumination and to the carrier mobility, which are therefore important parameters to maximize.

An often used quantity is the *fill factor (FF)*, which is the ratio between the maximum power $P_M = I_M V_M$ and the product $I_{SC} V_{OC}$. It describes how well behaved the I-V characteristics is (the more the curve approaches a rectangular shape, the better).

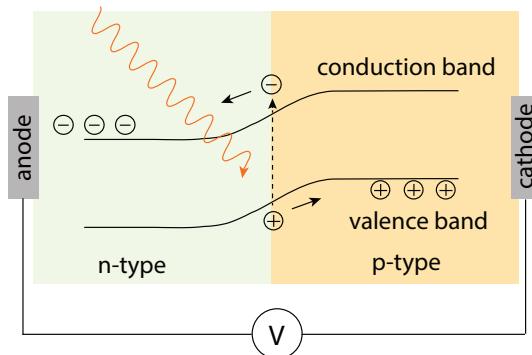


Figure 3.1: Principle of a solar cell using a p-n semiconductor junction.

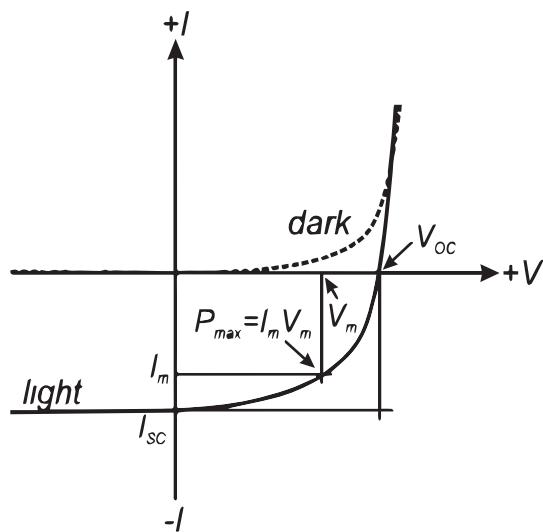


Figure 3.2: Typical I-V characteristics of a solar cell. SOURCE: [5, p.427]

Of practical importance for comparing solar cells is the power conversion efficiency η , giving the ratio of optical power which is converted into electrical power.

$$\eta = \frac{P_{max}}{P_{in}} = FF \frac{I_{SC}V_{OC}}{P_{in}}$$

Usually an optical source called AM1.5 is used, whose spectral intensity distribution matches that of sunlight reaching the earth's surface at an angle of 48.2°. [5, pp.426-433]

3.2 Solar Cells using QDs

Semiconductor nanocrystal solids, can be used for solar cells. Thus NCs made of CdSe, CdTe, PbSe, PbS and many more can be used for this purpose. Like with bulk semiconductors, heterojunction solar cells are possible (using materials with different band gaps), such as CdSe-CdTe cells [5, p.430]. Similarly, using Schottky-contacs is also an option.

Using NC solids made of QDs offers several advantages. One big advantage is the possibilty of choosing the size of the band gap by controlling the size of the QDs, which can be done easily during the synthesis of QDs. Controlling the band gap means essentially choosing the spectrum which can be absorbed, and consequently cells, which can make use of a broad spectrum, can be engineered.

Furthermore QD solar cells are easy to fabricate and that at low costs. Large-scale production would also be possible [5, p.447].

Using NC solids, there are promising perspectives for more advanced techniques, in order to increase efficiency. These invlove e.g. carrier multiplication (the absorption of one highly energetic photon causes the creation of multiple electron-hole pairs) or hot carrier solar cells (electrons in higher energy states in the conduction band are extracted before they relax to the band edge and lose some energy).

However, there are some problems which have to be overcome. One is the (air-)stability and lifespan of QD based photovoltaic cells. In many cases, the devices lose dramatically in efficiency after some time, which can be as short as hours or even minutes [10, p.26]. Another problem is the currently rather low efficiency of the cells (maximum acchived efficiency of around 7% for a PbS cell [1, p.1]). One issue leading to reduced efficiency is the presence of undesired states in the band gap (mid-gap or trap states). These arise due to 'dangling' (unbound) bonds of surface atoms, and are significant in a QD, since its surface to volume ratio is high. So-called *passivation* of the surface is thus very important.

Furthermore, for furture large-scale production, the materials used in the production process should be cheap, available in large quantities and preferably non-toxic, which contrasts with some NC materials that contain toxic elements like Cd or Pb.

3.2.1 Example of a PbS QD Solar Cell

Since the structure and fabrication methods of QD solar cell are quite diverse, we will focus here on a PbS QD solar cell, as they were produced at ETH in the Laboratory for Nanoelectronics [9]. Due to the small band

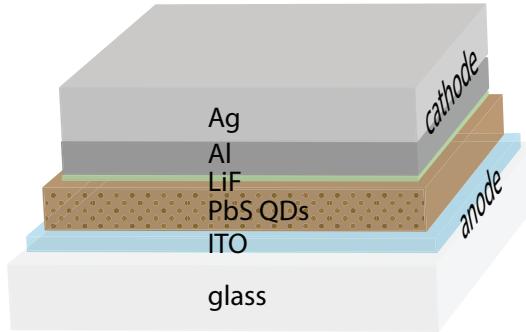


Figure 3.3: Structure of a PbS solar cell.

gap of PbS (0.37eV for bulk PbS), the solar cell is able to convert power from the near infrared spectrum. This is of interest, since roughly 50% of the solar energy that reaches the earth, is in the infrared spectrum.

Structure

The principle part of the cell is a Schottky junction of PbS and Al, with a thin protection layer (1 nm) of LiF in between. The Schottky barrier is responsible for the electric field which separates the photogenerated carriers. The Al cathode is covered by a layer of silver, for better air stability. The transparent anode is formed of a layer of indium tin oxide (ITO), on top of the PbS (figure 3.3).

Fabrication Process

The main steps involved in the fabrication are described below, as they were carried out in reference [9, pp. 13-19].

We start with a glass substrate, which is coated with ITO using lithography. The sample has then to be cleaned (using solvents, and afterwards by O_2 plasma treatment to remove organic residuals).

In the next step, the active layer, i.e. the PbS QDs, is deposited. This can be done by dip coating, where the substrate is immersed in a PbS-hexane solution, and taken out after a few seconds, leaving a thin film of the solution on the sample. Alternatively, spin coating can be used, where several drops of the PbS-Hexane solution are dropped on the substrate, which is then rotated to spread the drops, leading to a film of homogeneous thickness.

Now the long ligands surrounding the QDs have to be exchanged for short ligands, in order to improve inter-particle coupling (and thus e.g. carrier mobility). For this purpose, the substrate is immersed into a suitable compound: Ethandithiol, benzenedithiol (both organic), and ammonium thiocyanate (NH_4SCN , inorganic) can be used.

The sample is then rinsed in acetonitrile and or hexane. In order to obtain a PbS film of desired thickness, the steps of spin (respectively dip) coating, ligand exchange and rinsing have to be repeated several times.

In a last step, the cathode, i.e. the three layers of LiF, Al and Ag are evaporated on the substrate.

Chapter 4

Toolbox for OMEN in MATLAB (TOM)

The Toolbox for OMEN in MATLAB (TOM) was programmed to simulate spherical nanocrystals and to visualize the results of the simulations. Though we focused on spherical structures, the code is held abstract and slim in order to make extensions to other structures, such as nanowires, fairly easy. The main aim of TOM is to offer OMEN users a toolbox, which includes the following 3 main tasks:

1. Automatization of the OMEN simulation process

When it comes to simulating QDs with different parameters, users do not want to spend a lot of time on writing command files for OMEN and starting each OMEN task via the shell, but rather enter the main parameters into a Graphical User Interface (GUI) and let TOM do the rest (see section 4.3.2). This makes overnight simulations for large parameter sets possible.

2. Overview of all simulations done in the past

All information respectively parameters of past simulations can be displayed in a GUI. Exporting selected simulations and visualizing them is possible as well (see section 4.3.3)

3. Visualization of simulation data

Different kinds of plots are available within the toolbox, such as visualizing band gaps, wave functions or quantum dot structures (see section 4.3.4).

4.1 Installing the Software

You can get a version of TOM at the Laboratory for Nanoelectronics (LNE) at ETH Zurich. Copy the folder TOM to any directory on your computer. Now it is necessary to define some paths. Open therefore TOM/System/initTOM.m and change all fields, that are listed below. The field *root* contains the path, where the folder TOM is saved. Similarly, the paths of the simulations folder and of the OMEN executable are stored in the corresponding fields. Note that these paths do not have to direct to a subfolder or TOM, i.e. simulation data can be stored anywhere on the computer.

```
config.root      = '/usr/home/TOM/';
config.OMEN       = [config.root, 'OMEN_ethz-amd64'];
config.vOMEN     = '04May2013';
config.simulations = [config.root, 'Simulations/'];
```

4.2 Using a newer version of OMEN

If you would like to use a new version of OMEN , please make the following changes. Open the TOM/System/initTOM.m file and change config.vOMEN to the date of the new version's release. Afterwards copy the new OMEN executable to the path defined in config.OMEN. It might be possible that simulations do not run with the new executable, as the rights are not set to *executable*. In this case, right click on the executable, select properties and afterwards *Run as executable*.

4.3 Using TOM

4.3.1 Basic concept

The first step when you want to work with TOM is its initialisation. Therefore add the TOM folder including subfolders to the MATLAB path, type `initTOM.m` in the command window and hit enter.

The command `help TOM` will provide you with all available functionalities including a description how to use them. Another way to get help is by opening the TOM manual, which can also be accessed via the help command or the menu lists in the GUIs.

Table 4.1 gives a quick overview of the most important function parameters, that are used regularly in the TOM code.

Parameters for the simulation are stored and passed as objects to functions of the class *Qdot*, further referred to as Quantum Dot Object (QDO). The class provides properties for all parameters necessary for the simulation, as well as properties for administrative purposes, such as the specific simulation folder. Parameters relating to the geometry are stored in an object of subclass *Geometry*. Since more than one material is possible, the geometry property is often an array of objects of class *Geometry*. To instantiate a QDO, one can call the constructor with no arguments, which will create an empty QDO. Alternatively, a string with the material name can be passed as an argument, in which case the new QDO will be constructed based on parameters defined in an external file, located in the folder *Classes*. The class *Qdot* provides some methods for basic displaying of some selected parameters, such as *getSelParams*.

Example. Creating a *Qdot* object based on default parameters and set the radius to 4

```
myQdot = Qdot('Cds_CdSe');
myQdot.geometry(2).radius = 4;
```

DIR	Directory path
EDO	Experimental data object
EDOA	Array of experimental data objects
QDO	Quantum dot object
QDOA	Array of quantum dot objects
propertyName	Property name of an EDO or QDO
BGap	Band Gap
NMod	Number of modes
NOrb	Number of orbitals
band	CB: Conduction band or VB: Valence Band
tol	tolerance

Table 4.1: Important function parameters

4.3.2 Running a simulation

Type `gui_simulate` in the MATLAB command window and hit enter. The window as in figure 4.1 will open. A simulation set is defined as one row of the table, i.e one material with all kinds of sweeps. You can add more simulation sets by using the *Add rows to the table* panel. It is possible to copy and paste single cells of the table using the appropriate short cuts of your MATLAB default keyboard setup (`CTRL+C` & `CTRL+V` Windows setting, `ALT+W` & `CTRL+Y` Emacs setting). The columns are filled as follows:

1. Material

Enter the number for the material you would like to simulate, according to the *Material / Compound* list.

Material Name_lent Simulations done with tight binding parameters by Lent
Material Name_allan Simulations done with tight binding parameters by Allan

2. Geometry

Enter the number of the geometry given in the *Geometry* list. Very important in the case of materials with shells is, that you have to enter the geometry type of the core and the shell. The geometry types are separated with a comma.

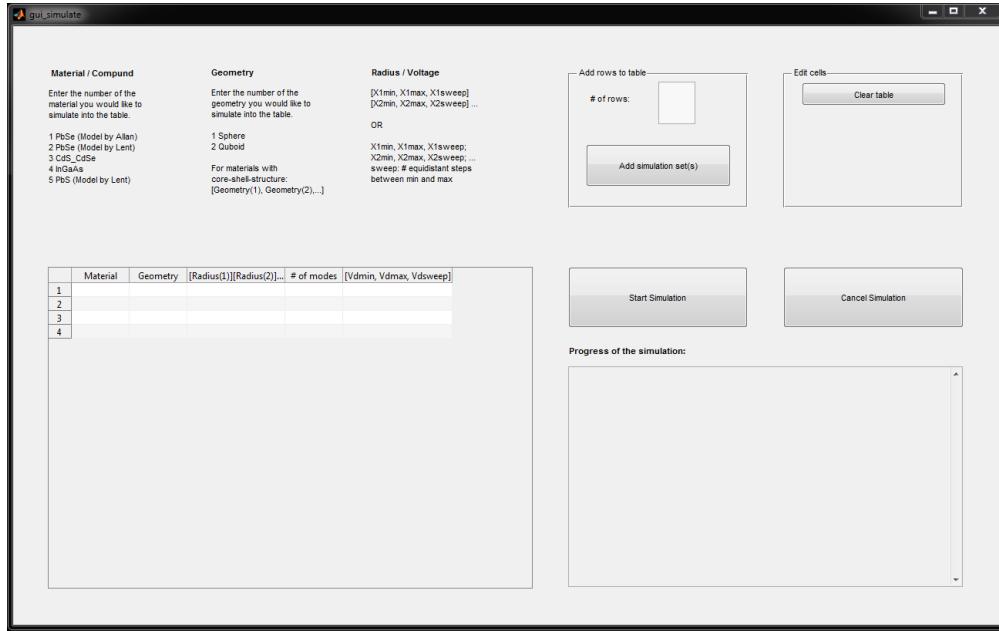


Figure 4.1: The gui_simualte window

Example. For a spherical CdS-CdSe quantum dot the cell would look like this: 1, 1

3. Radius [nm]

The radius has to be entered in a specific way. The syntax is:

[Rmin(1), Rmax(1), Rsweep(1)] [Rmin(2), Rmax(2), Rsweep(2)] ...

Rmin(i) smallest radius of the ith material to be simulated

Rmax(i) largest radius of the ith material to be simulated

Rsweep(i) number of equidistant points between Rmin(i) & Rmax(i)

Example. For the simulation of a single spherical PbS quantum dot with radius 3.5 nm you would enter: [3.5,3.5,1]

4. # of modes

Enter a number of modes you would like to calculate.

5. Electric field in units [V/nm]

The electric field parameter is entered in the same way as the radius. You find more information under the remark below.

6. update_bs_target

For higher electric fields OMEN cannot differentiate conduction and valence band, therefore the user has to make a guess where the band gap might be. OMEN will then simulate the # of modes around this given energy (bs_target). If you would like to make use of this option enter 1 in the update_bs_target field otherwise 0. Please note, that if you choose 0, you will have to enter any numerical value (e.g. 0) in the bs_target field as well, otherwise the GUI cannot process the data.

7. bs_target [eV]

The energy value around which the energy levels are calculated.

8. Permute

Enter 0, if the radii vectors should be combined element wise, i.e. first element of R(1) and R(2) give a simulation, second element of R(1) and R(2) give a simulation and so on. Each radius pair will be simulated with all possible electric fields specified. Selecting 1 will permute all possible radii with each other and all electric fields.

Example. For a spherical CdS-CdSe QD the input cell would look like this: [1,4,4][5,6,2]

If you select Permute = 1, TOM will calculate all possible permutations and generate therefore 8 quantum dots:

Quantum dot	1	2	3	4	5	6	7	8
Core radius in nm	1	1	2	2	3	3	4	4
Shell radius in nm	5	6	5	6	5	6	5	6

Example. For a spherical CdS-CdSe quantum dot the input cell would look like this: [1,2,2][3,4,2] If you select Permute = 0, TOM will combine elementwise the entries of the two vectors:

Quantum dot	1	2
Core radius in nm	1	2
Shell radius in nm	3	4

Remark (Vectors & Matrices). As the MATLAB GUIs do not directly accept vectors or matrices in standard MATLAB syntax, the parameters have to be entered as a string and are converted to matrices later on.

There are different ways to enter the parameters. Use the one that is the most clear for you.

<code>a,b,c,...,d</code>	<i>or</i>
<code>[a,b,c,...,d]</code>	becomes a double vector

$$V = [\ a \ b \ c \ \dots \ d]$$

<code>[a,b,c] [d,e,f] ... [g,h,j]</code>	<i>or</i>
<code>a,b,c; d,e,f; ...; g,h,j</code>	<i>or</i>
<code>[a,b,c; d,e,f; ...; g,h,j]</code>	becomes a double matrix

$$\begin{matrix} M = [& a & b & c \\ & d & e & f \\ & \cdot & \cdot & \cdot \\ & g & h & j \end{matrix}$$

where `a,b,...,j` are doubles as **strings**.

These input styles can be applied to the columns *Geometry*, *Radius* and *Voltage*.

You can use as many spaces as you want in between. The first and the last brace are not necessary if only a vector is entered or if rows are separated by semicolons.

After entering all the necessary parameters proceed by clicking Start Simulation. The *Progress of the simulation* panel will keep you informed about the warnings, wrong entered parameters and the current status of the simulation.

4.3.3 Display simulation information

There are two ways of displaying simulation information. Either you can see the whole database (all simulations that are stored in the Simulations folder) or only specific data, for example only PbS simulation data.

Remark. TOM uses objects (called *qdotObj*) to store all important data of simulations such as the simulation parameters, date of simulation etc. All operations are done using these objects or arrays thereof (QDOA). How to create such an array is described in section 4.3.5.

Displaying the whole database can be done by typing `gui_db` into the MATLAB command window. A window as in figure 4.2 will appear showing all parameters and technical information of each simulation. Please note, that according to the size of the database, it might take some seconds to load all data. If you only want to display simulation data for QDOs in a QDOA, you can also call `gui_db(QDOA)`.

Within the GUI you can sort the simulations with the column header, select simulations and plot them, open the directory of a simulation or even export a selection, which is then available as an Quantum Dot Object Array (QDOA) in the main workspace entitled *ExportedDB*.

4.3.4 Plotting

Here follows a short description of functions, which can be used for basic visualization of the data obtained by the OMEN simulation. For a more detailed description, please refer to the code. Note that these functions are based on the directory structure created by the simulation function `simAll.m`, i.e. to work properly, the simulation data, as well as the corresponding QDO must be located in their own folder, with the folder name specified in `QDO.path` property.

would be recommendable.

```
function compareEV(QDOA, band, NMod, tol, propertyName, showGrid)
```

Plots the same as *plotEVAlongAxis*, but for three different directions (x, y, z-axis), and arranges them in subplots in one figure.

Plotting energies

```
function plotBandGap(QDOA)
```

Plots the band gaps of a QDOA in dependence of radius and applied voltage. Calling the function without an input argument, will create plots for the whole database.

```
function plotEnergyLevels(QDOA)
```

Plots all simulated energy levels of an array of QDOs and highlights the band gap.

```
function plotVoltBandGap(QDOA)
```

Plots the band gap against voltage for a constant radius. The QDOs must have the same radius/radii.

4.3.5 Additional tools

In order to know which parameter sets have already been simulated, there are some useful tools, which can be found in the folder *Functions/QdotUtils*. The basic principle is to get all parameters which were simulated, which can then be displayed in the GUI, filtered, deleted and so on.

Getting the parameters from all simulations

```
function getQDOA()
```

This is done by loading the QDOs of all performed simulations from their folders, and storing them in a QDOA.

Filtering

```
function filtered = filterQDOA(QDOA, propertyName, value, mode, tol)
```

The filtering can be applied to any QDOA, and returns a subset of this array, matching specified criteria. The argument *propertyName* specifies the *Qdot* property which is compared to *value*. The filter criteria are specified by selecting a mode of filtering. The following filtering modes are available:

1. The property exactly matches *value*.
2. The property lies within a range of values, specified by a vector: *value* = [min max]
3. The property approximately matches *value*. For numeric properties this is specified using a tolerance. For string properties the *value* should be a substring of the property.
4. Filter for a constant difference between two properties. The property names are specified in a cell array: *propertyName* = {*propertyName1*, *propertyName2*}
5. Filter for a constant ratio between two properties.

The last two modes are especially interesting for selecting QDOs with two or more materials, to find the objects with a specified shell-thickness.

Example. Filter for QDOs with different properties:

- selection 1: only QDOs with radius = 3.5nm

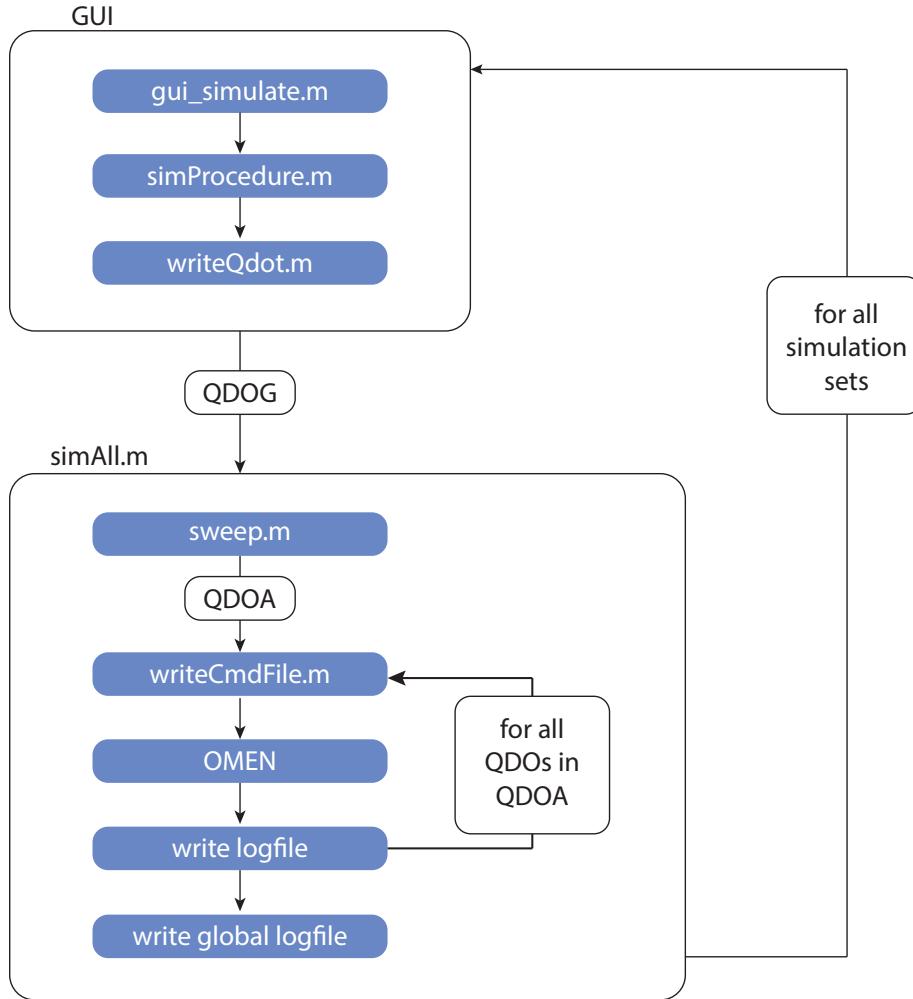


Figure 4.3: Workflow of the simulation procedure.

- selection 2: only QDOs with a constant difference of 0.7nm (with a tolerance of +/- 10%) between radius of material 1 and radius of material 2.
- selection 3: only QDOs with a material containing Pb.

```

myQDOA = getQDOA;
sel1=filterQDOA(myQDOA, 'geometry(1).radius', 3.5, 1, 0);
sel2=filterQDOA(myQDOA, { 'geometry(1).radius', 'geometry(2).radius' }, 0.7, 4, 0.1);
sel3=filterQDOA(myQDOA, 'mat_name', 'Pb', 2, 0);

```

4.4 Maintaining TOM

4.4.1 General Structure

TOM stores all files of one simulation in a folder. To avoid conflicts in the data storage, the folder names are bijective. They have the following form: `IDyyyymmdd-hhmm-ssffff_MATNAME`. The name contains the date and time (including milliseconds) when the simulation was started as well as the name of the material, that is simulated. Figure 4.5 illustrates the structure of a simulation folder. Note, that if you simulate with parameter `update_bs_target = 1`, OMEN will not create files for valence and conduction band, but rather write all eigenenergies into `VB_E_0_0.dat` or `CB_E_0_0.dat`. If you would like to make changes in TOM or add new structures, such as nanowires, it is useful to get familiar with the workflow of the the software. Figure 4.3 illustrates the process.

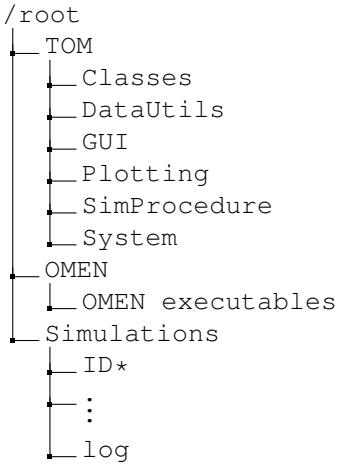


Figure 4.4: The TOM structure by default

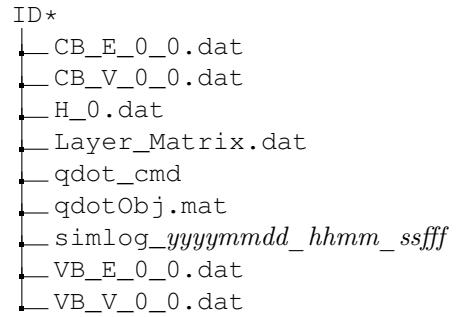


Figure 4.5: Structure of a simulation set

4.4.2 Simulation

The simulation parameters entered in the GUI are passed to a function, which will then start the simulation with OMEN. The parameters are stored in QDOs. Since it is often desirable to simulate over a range of parameters, some parameters (i.e. the radii and the electric field) are at this stage not scalars, but vectors, containing starting value, end value and number of steps in between. Such a generic QDO is further referred to as QDOG.

The QDOG is passed to the function *simAll.m*, which will simulate all desired parameter combinations, by performing the following steps:

1. An array of QDOs (QDOA) with all combinations of the parameter is created in the function *sweep.m* from the QDOG. Supported sweep parameters are currently radius and electric field. This could easily be extended to other parameters by modifying the function *sweep.m*.
2. The elements in the QDOA are then simulated one after the other, and all generated data is saved in separate folders, named *IDtimestamp_material*:
 - (a) The OMEN command-file *qdot_cmd* is written, using the function *writeCmdFile.m*.
 - (b) The OMEN simulation will be started using the MATLAB function *unix*, which calls the operating system, to execute the specified command.
 - (c) A logfile is written, recording the duration and the success of the simulation, as well as the console output of OMEN. The success of the simulation is checked by inspecting whether the desired files were created.
3. After the simulation of all elements in the QDOA, an additional logfile is written, and saved in the folder *log*. It gives information about the success of all simulations, and thus provides an easy way to check if (and which) simulations failed.
4. Returned to the calling function is the QDOA, as well as a vector indicating the success of every simulation.

Note that it is not strictly necessary to start the simulations using the GUI. The QDOG containing the desired parameters can also be created with standard MATLAB syntax, and passed subsequently to the function *simAll.m*, as is shown in the following example.

Example. Simulate PbS quantum dots with radii 1.5, 2, 2.5, 3nm.

```

myQdot = Qdot('PbS_lent');
myQdot.geometry.radius = [1.5 3 4];
simAll(myQdot);
  
```

4.5 Q & A

Why is opening gui_db is not possible? It might be that there are failed simulations in the database. Please delete the corresponding folders and try again.

How can I stop the simulation? MATLAB is blocked during the simulation process. You might have to abort the process by pushing CTRL+C a couple of times.

Why does the simulation not start? You might have to make to set execution rights for the OMEN executable: Tick 'Run as' after right clicking the OMEN executable and selecting properties.

Chapter 5

Analysis of PbS QD simulation data

In this chapter we will take a look at the simulation data, which are based on a tight-binding model used by OMEN . The parameters used for the simulation can be found in appendix B on page 33. We will make an analysis of the energy levels and wave functions of PbS QDs and draw some conclusions.

Remark. There are a few practical aspects to note concerning the simulation of PbS QDs with OMEN: Since OMEN will consider in its calculation 18 orbitals for the atoms, one must keep in mind that the simulation uses significantly more computing resources than a simulation of a CdSe-CdS QD for instance. Especially the memory usage during the calculation can easily exceed 10GB for larger QDs. The size of the generated simulation data for one QD can also amount to more than a few 100MB. It has to be kept in mind, that the number of atoms scales with the third potence of the radius. Another problem is the high degeneracy of energy levels. This makes it necessary to simulate a higher number of modes, thus increasing the usage of resources further.

5.1 Energy levels

Remark. In the following discussion, the terms conduction band, band edge and so on are used. Although there are no energy bands present in a QD, but rather discrete energy levels, these terms nevertheless make sense, since the states above the band gap are similar to conduction band states, and those below to valence band states, respectively. Indeed, if the QD gets bigger, we finally reach the limit where we can treat it as a bulk material. The term *conduction band* refers in this context to the discrete energy states above the band gap.

Taking a look at the eigenenergies close to the bandedge, one can see that there are 8 closely spaced modes, for conduction and valence band respectively. Generally, closest to the band edge there is a twofold degenerate energy level, followed by a fourfold degenerate level and then again a twofold degenerate level. (For a few simulations the order is different, for example the fourfold degenerate energy level is closest to

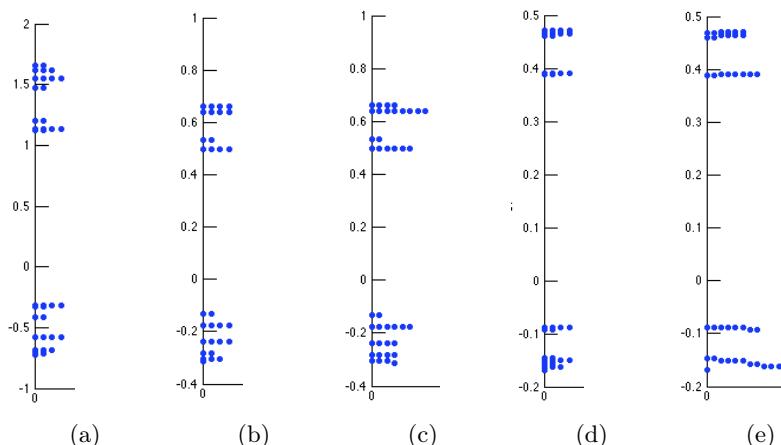


Figure 5.1: Energy levels for different sized QDs: 2nm (a), 6nm (b) and (c), 10nm (d) and (e). Vertical axis in eV. Multiple dots on the horizontal axis signify degeneracy. In plots (c) and (e) energies within 0.03eV are plotted as degenerate, for better visibility.

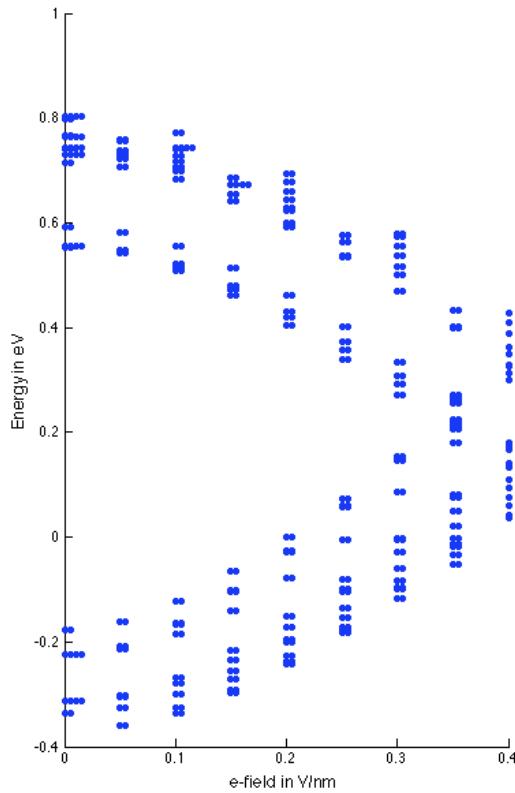


Figure 5.2: Energy states (including degeneracy) for different electric fields.

the band edge.)

As the size of the QDs increases, the energy levels get closer to each other, resulting in higher degeneracy. This is shown in figure 5.1 (a),(b),(d), where the energy levels (including degeneracy) are shown for 2, 6 and 10nm QDs. Since some levels are very closely spaced, they are not clearly distinguishable from each other. For this reason, the tolerance, within which an energy level is shown as degenerate, was increased in figure 5.1 (c),(e). An effective eightfold degeneracy for the 10nm QD is now clearly visible.

In the presence of an electric field, this degeneracy is broken, leading to more energy levels, which are all, interestingly, twofold degenerate. This is shown in figure 5.2 for a 5nm QD, where the energy levels are plotted against an applied electric field. One can clearly see how the band gap gets smaller, as is discussed later on.

5.2 Band gap

All band gaps of our PbS simulations are plotted in figure 5.3. Furthermore, we have fitted the $1/R^2$ dependence of equation 1.1 to all band gaps where no voltage was applied. As we can see from the graph, the bulk band gap of lead sulfide (PbS) should approximately be 0.46eV, which means a pretty big deviation from experimentally determined values of 0.37eV at 302K (see appendix A). We have made the same observations while comparing other experimental values with simulation data. As experimental data, transmission electron microscopy (TEM) images, absorption and PL spectra (see figure 5.4, 5.5 and 5.6) were available. From the TEM images, average particle sizes were measured and compared with approximately equivalently sizes from simulations. The results are listed in table 5.2. Significant deviations can be noticed between experimental and simulated data, which are reasoned in three significant error sources, that explain the deviations. First of all, the synthesis does not deliver perfect spherical and homogeneous QDs, which causes the broadening of the spectra. Second: it is very difficult to determine the size of the QDs from the TEM images, especially without sophisticated software. This might lead to comparison of experimental and simulated values, which actually do not belong to each other. Third: comparing measurements of the real physical world with simulations. There might be errors in the measurement apparatus, impurities in the QDs and disregarded effects in the simulation, which have an impact in reality.

Remark. All experimental data used in this section were provided by the LNE at ETH Zurich.

	$\sim 2.97\text{nm} - 3\text{nm}$ PbS - 261	$\sim 3.21\text{nm} - 3\text{nm}$ PbS - 61	ϕ - Simulated ϕ $\sim 3.95\text{nm} - 4\text{nm}$ PbS - 190	$\sim 4.97\text{nm} - 5\text{nm}$ PbS - 220
Energy at PL peak	1.4529eV (853nm)	1.2256eV (1012nm)	n/a	1.0040eV (1235nm)
Band gap experimental	1.7487eV (709nm)	1.5194eV (816nm)	1.2808eV (968nm)	1.0489eV (1182nm)
Band gap simulated	0.9929eV	0.9929eV	0.8645eV	0.7296eV

Table 5.2: Comparison of experimental and simulated band gaps.

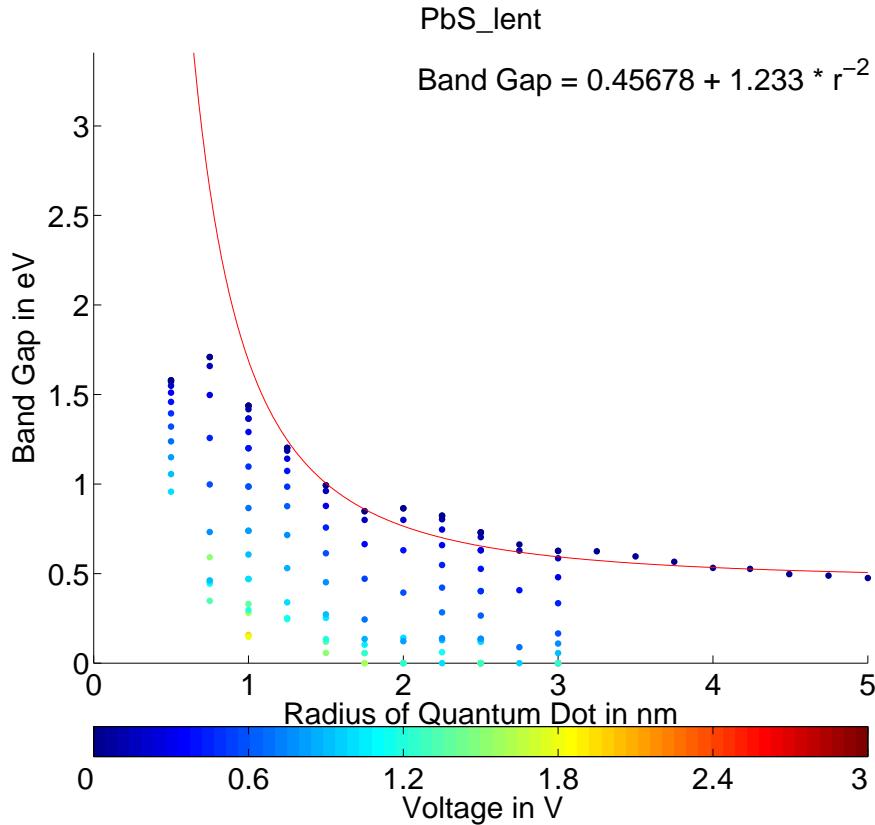


Figure 5.3: PbS band gaps against radius of all simulated QDs. The color indicates the applied voltage.

5.2.1 Band gap of QDs with an applied voltage

In figure 5.8 we can see, that with increasing voltage the band gaps approach a zero value. Interestingly, this does not happen linearly, for every constant voltage increment. By visualizing this effect for constant radii (figure 5.7), we recognize that the energy gap drops in a parabolic way until it completely reaches the zero value. Furthermore, we recognize in figure 5.8 a shift of all energy levels towards each other.

5.3 Wave functions

5.3.1 Shape of the wave functions

QDs bigger than 3nm

Remark. Although the term *wave function* appears a lot in this section, the term is rather meant in the sense of *probability density*, since the plots, on which the analysis is based, are more easily interpreted if they show probabilities instead of complex numbers.

Sometimes, the wave functions of QDs are described in analogy to atomic orbitals, labeled S, P, D and so on, with subscript e or h, denoting electron-like (conduction band) states or hole-like (valence band) states

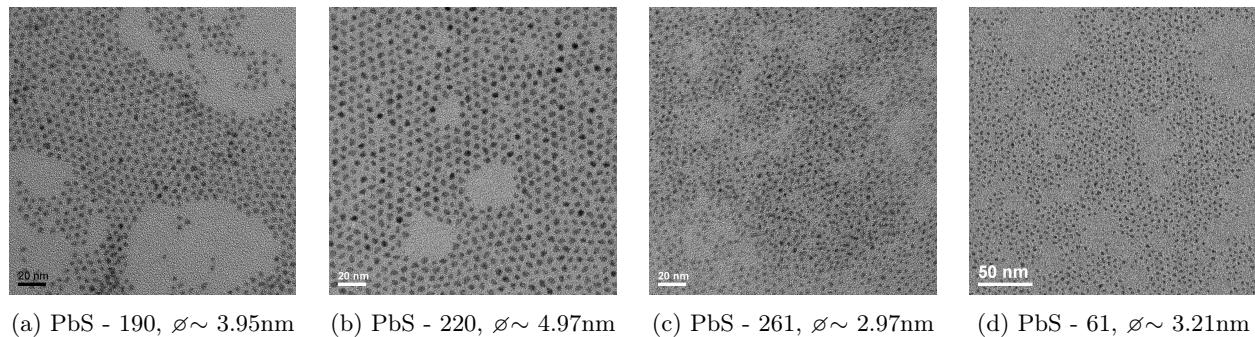


Figure 5.4: TEM images of PbS QDs

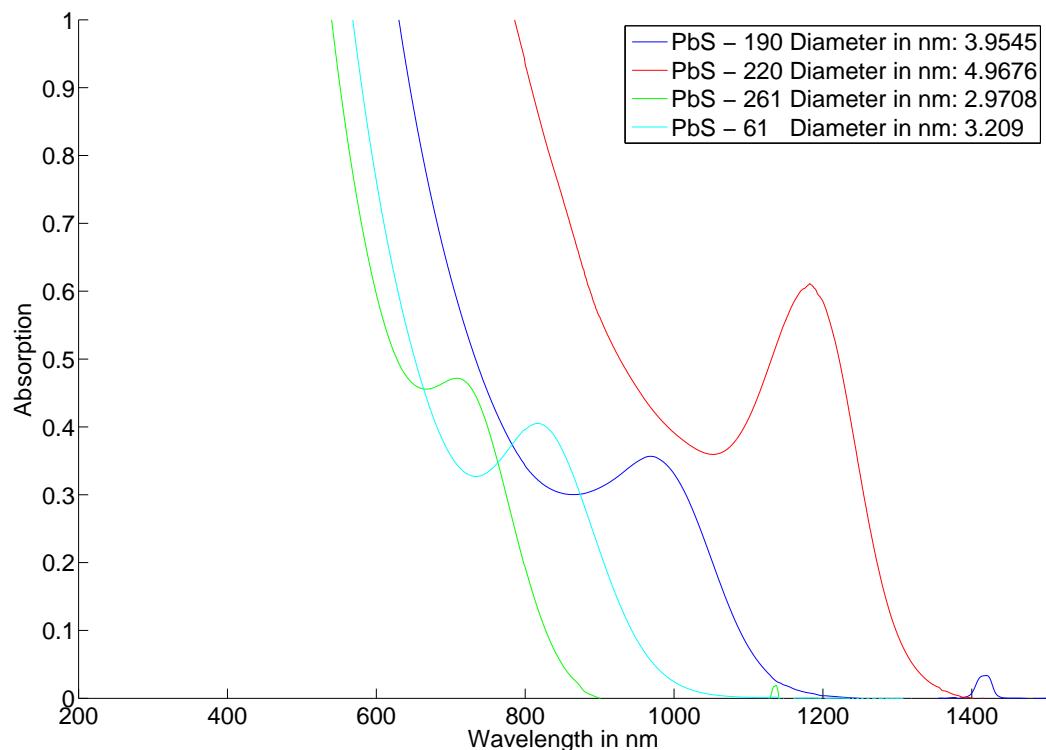


Figure 5.5: Experimentally determined absorption, plotted against wavelength in nm for 4 synthesized PbS QDs.

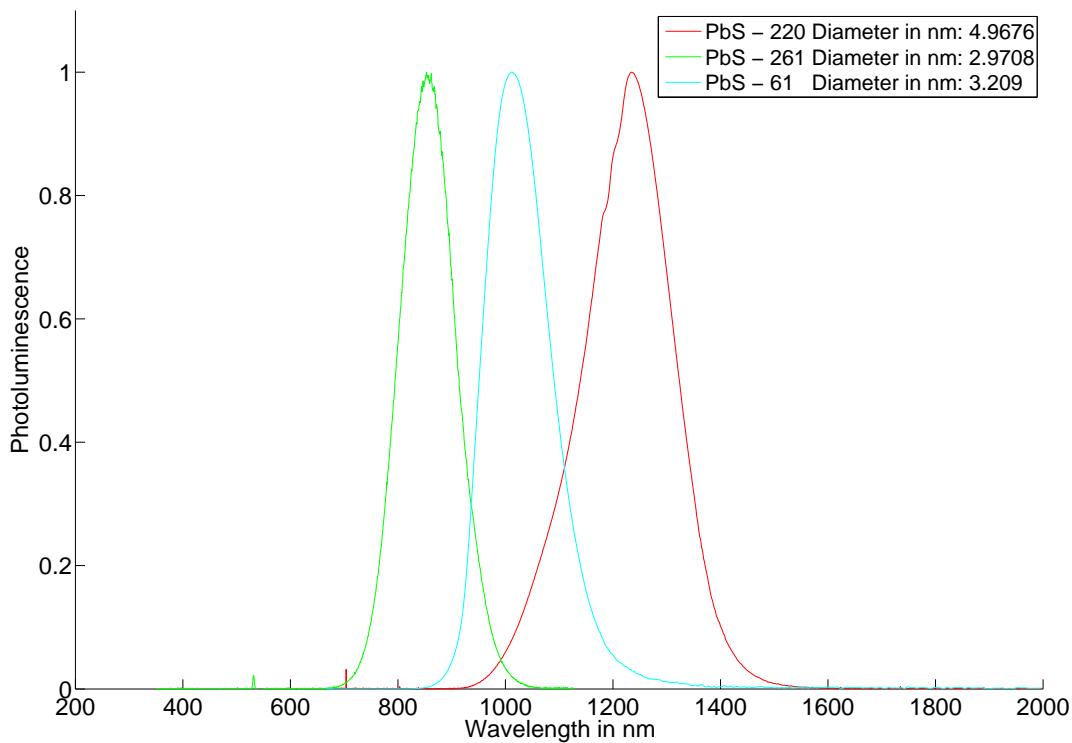


Figure 5.6: Experimentally determined PL plotted against wavelength in nm for 3 synthesized PbS QDs.

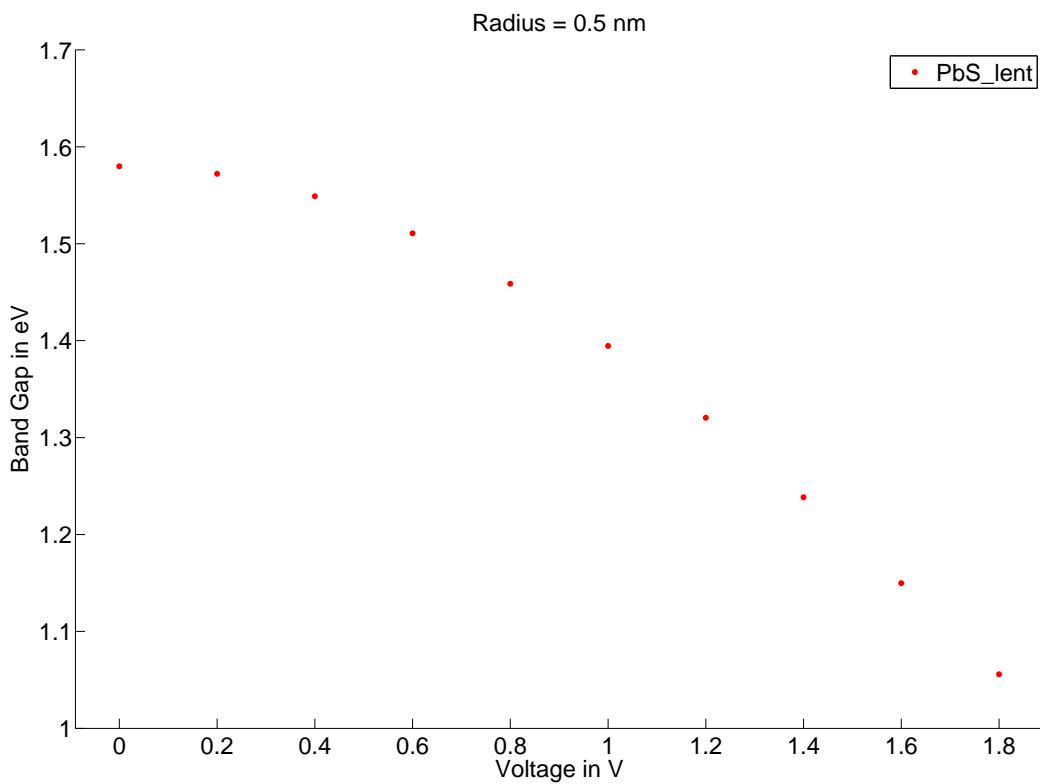


Figure 5.7: PbS band gaps plotted against voltage with constant radius 0.5nm.

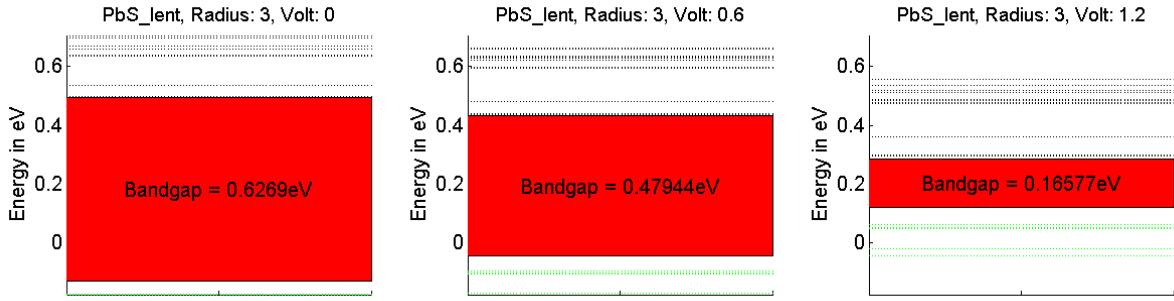


Figure 5.8: PbS energy levels for different voltages with constant radius 3nm.

plotID: 1, mat: PbS_lent, Efield: 0, ModNr: 6, E-Level: 0.437598 eV

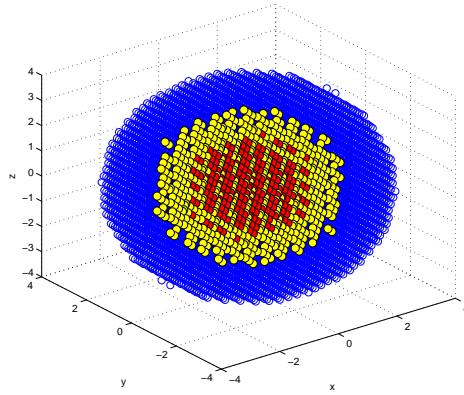


Figure 5.9: Probability density for an energy state in the lower conduction band of an 8nm QD. Locations of very high probability are shown in red, those of medium to high probability in yellow, such that the sum of the probabilities of all yellow and red locations is 50%. Note that in following figures, different probability values may be used, for better visibility.

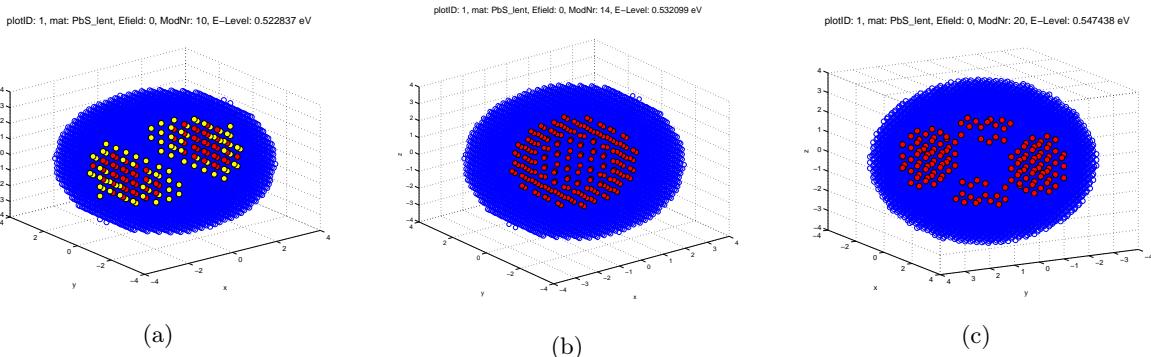


Figure 5.10: Probability density for higher energy states in an 8 nm QD: barbell-shape (a), spherical shell-shape (b), crossed barbell-shape (c). In plots (b) and (c) the locations of medium high probability (yellow points) are not shown for clarity.

respectively. We will see how well this picture corresponds to the simulation.

The 8 energy states ('modes') closest to the band edge (for conduction and valence band respectively) have wave functions with spherical symmetry, where the highest probability density is in the center (figure 5.9). This is in agreement with the 8 predicted $1S_{e,h}$ orbitals for PbS [5, p.410].

The higher energy states show wave functions with more complex shapes. For example, a 8nm QD shows the following wave function shapes: After the 8 spherical conduction band states follow 4 (degenerate) states with barbell shape, in different orientations. Then 2 states with spherical shell shape. After that, 2 states with a shape similar to two crossed barbells. Then again 2 spherical shell-like states, followed by 2 ring-shaped wave functions, and so on (figure 5.10). For the valence band states, the shapes are similar, although they do not occur in the same order (the same is true for QDs of different sizes).

QDs smaller than 3nm

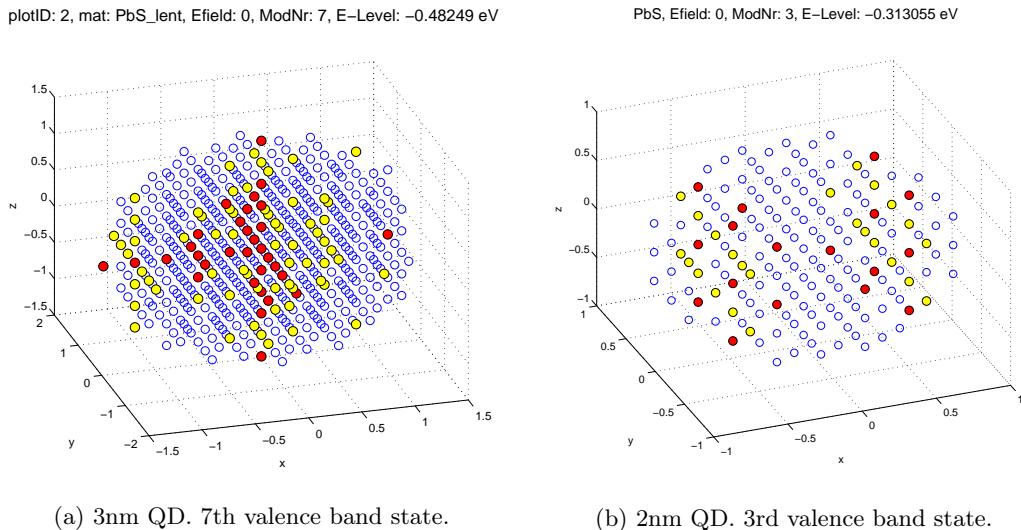


Figure 5.11: Probability density for valence band states. The shape starts to deviate from the previously spherical shapes.

For QDs smaller than 3nm, the problem is that it is more difficult to see the shape of the wave function (too few atoms). Furthermore it is not clear how well this models a real QD, since the surface (and thus passivation of the surface) begins to have an even bigger influence.

For 2 and 3nm QDs, the 8 lowest conduction band states still remain more or less spherical. Whereas the valence band states start to lose spherical symmetry. For a 3nm QD, mode 7 and 8 are already slightly asymmetric (figure 5.11 (a)), and for the 2nm QD, even the modes 1 to 4 are clearly not spherical, but the wave function is rather localized at two sides (figure 5.11 (b)).

5.3.2 Influence of an electric field

The presence of an electric field results in a shift of the wave function, i.e. the maximum of the probability density is not in the center anymore and the spherical symmetry of the 8 first states is broken (for conduction and valence band respectively). Furthermore, one can see that the valence band states really behave differently than conduction band states: The wave function is shifted in the opposite direction (figure 5.12). This confirms that the valence band states are hole-like, similar to bulk semiconductor band theory.

For larger electric fields the band gap gets smaller, until it finally disappears, i.e. conduction and valence band states are not separated anymore. For example, for a 5nm QD, the band gap disappears for electric fields larger than 0.35 V/nm (figure 5.2). The states close to the (former) band gap cannot be separated in conduction and valence band: as energy increases, some hole-like states are followed by electron-like (i.e. conduction band-like) states, which in turn are followed by hole-like states and later again electron-like states (figure 5.13).

Additionally, with higher electric fields, the wave functions seem not only to be shifted, but change shape: Some now look more like asymmetric barbells or even stranger, ring-like shapes (figure 5.13 (a) and (f)).

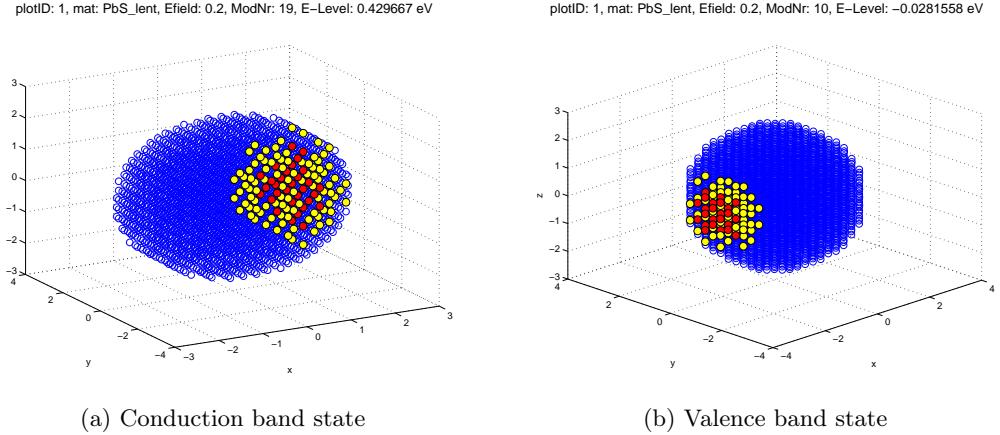


Figure 5.12: Probability densities for a 5nm QD in an electric field of 0.2V/nm.

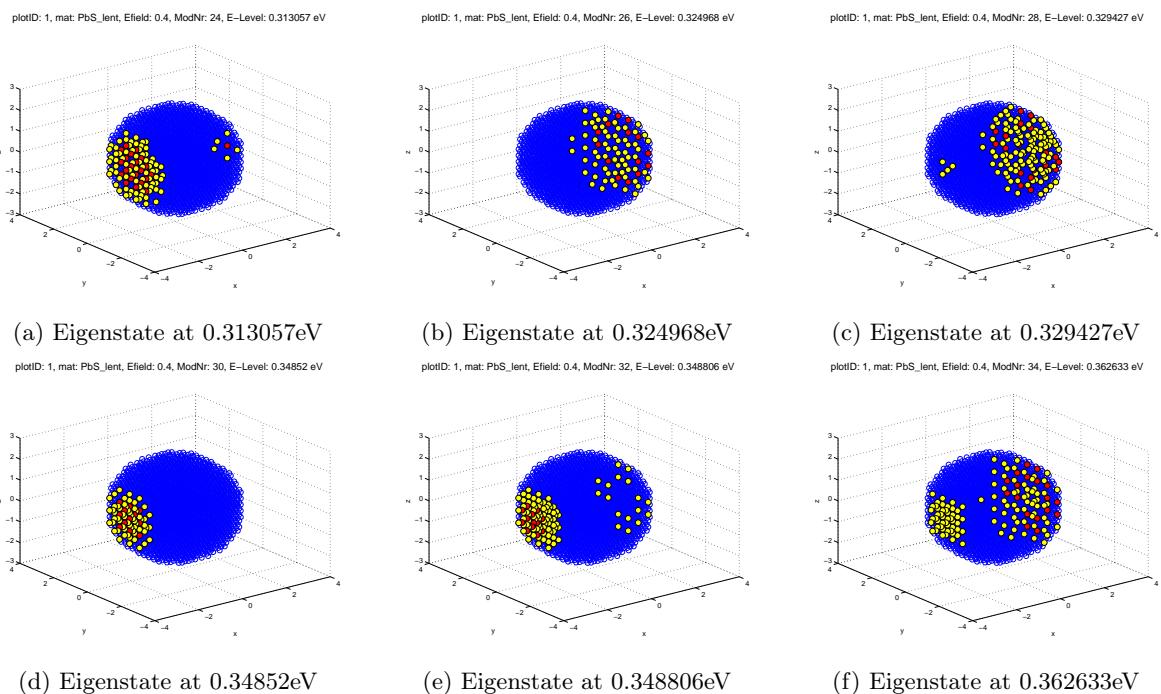


Figure 5.13: Probability densities in the presence of a high electric field (0.4V/nm). Increasing energy from (a) to (f). Hole-like states (a),(d),(e) become mixed with electron-like states (b),(c),(f).

5.4 Conclusions

We have seen that larger PbS QDs have eightfold degenerate energy states at the band edges, whose wave functions have spherical symmetry. Higher energy states show more complex wave functions. For QDs smaller than 3nm, the eightfold degeneracy is lost more and more, as well as the spherical symmetry of these wave functions. However, it is questionable how close to reality the simulations of very small structures below 2nm are. Under the influence of an electric field, the wave functions shift, according to their being hole- or electron-like, in opposite directions.

Furthermore we noticed, that the band gap is depending on size and the applied voltage. Increasing the voltage, energy levels get closer and cause a narrowing of the band gap.

Appendix A

Lead sulfide (PbS) parameters

A.1 Basic characteristics

Lead sulfide is an inorganic compound.

Molecular formula	PbS
Molar mass	239.30 g/mol
Density	7.60 g/cm ³
Melting point	1118°C, 1371 K
Boiling point	1281°C, 1554 K
Index of refraction	3.91
Crystal structure	rocksalt
Lattice constant	5.936 Angstrom
Energy gap	0.37 eV at 302K

Table A.1: Properties of PbS

A.2 Tight binding parameters

Our simulations are based on tight binding parameters determined by Craig S. Lent et al. in year 1986 [3].

$E_{s,c}$	$E_{s,a}$	$E_{p,c}$	$E_{p,a}$	$E_{d,c}$	$E_{d,a}$					
-6.546	-13.827	3.486	-1.153	9.27	10.38					
λ_c	λ_a									
1.559	-0.211									
$V_{s,s}$	$V_{s,p}$	$V_{p,s}$	$V_{p,p}$	$V_{p,p\pi}$	$V_{p,d}$	$V_{p,d\pi}$	$V_{d,p}$	$V_{d,p\pi}$	$V_{d,d}$	$V_{d,d\delta}$
-0.364	0.936	0.186	2.073	-0.281	-1.142	1.16	-1.54	0.517	-1.67	0.659

Table A.2: Nearest-neighbor tight-binding parameters of PbS in eV

Appendix B

Simulation Parameters

The parameters which were used for the simulation of PbS QDs are listed in table B.1. For detailed description of the OMEN parameters, refer to the OMEN manual [13].

OMEN parameter	Value	Description
mat_name	PbS_lent	Material
a0	0.5936	Lattice constant
lattice_type	rocksalt	Crystal structure
dsp3	30	Passivation energy (surface) [eV]
tb	20	Tight-binding order
first_atom	cation	Atom situated at coordinates [0 0 0]
open_system	0	0 for a closed system
max_bond_def	0.1	Maximum relative bond deformation
n_of_modes	20	Number of modes
Vdmin		Minimum voltage applied on structure [V]
Vdmax		Maximum voltage applied on structure [V]
NVD	1	Number of different voltages
x	[1 0 0]	
y	[0 1 0]	
z	[0 0 1]	
no_mat	1	Number of pieces forming the structure
no_channel_mat	1	
no_oxide_mat	0	
mat_type(1)	sphere	Geometry of material 1
mat_cs(1)	yes	
mat_id(1)	1	Material 1
mat_coord(1,1)	[0 0 0]	Center of material 1 structure
mat_radius(1)		Radius of material 1 [nm]

Table B.1: Simulation parameters for OMEN. Where no value is specified, simulations for different values were performed.

Glossary

Colloid Colloids are particles or droplets with a diameter of about 1-1000nm, that are dispersed in another medium, which can be a solid, gas or liquid. 34

Colloidal Quantum Dot Quantum Dots that have been created by a chemical solution process (see chapter 2). 34

Monodispersity A collection of particles with same size, shape or mass is called monodisperse. 34

Monomer Monomers are molecules that can take part in chemical reactions. They can connect themselves and form molecular chains, or polymers. 34

Nucleation Nucleation is the process of strongly localized phase changes in a substrate around focal points (nuclei). The nucleus often grows exponentially with time. Speaking in terms of crystal formation, this means, that atoms, ions or molecules in a solvent respectively liquid form a solid crystal. 34

Ostwald rippening Is an autonomous running process in disperse matter (for example liquid sols) with inhomogeneous particles. Here smaller particles dissolve and get attached to bigger ones. 34

Phase The term phase as understood in material sciences, thermodynamics and physical chemistry is a region, where the chemical composition of matter is homogeneous under certain circumstances. Often, the phase is related to the state of matter, e.g. water is of a constant phase for temperatures below the freezing point. 34

Precursor Precursor is a compound that is needed for a chemical reaction during a synthesis. 34

Surfactant A surfactant is a molecule, that is dramatically absorbed to the surface of the growing QD under the reaction conditions [15]. 34

Transmission electron microscopy A transmission electron microscope is a high resolution microscope, that uses an electron beam to produce an enlarged image of a sample. The beam impacts the ultra-thin specimen and the transmitted electrons form an image that gets enlarged to make it visible for the human eye. Usually the samples have to be prepared very carefully, as the electrons interact with the specimen. 34

Acronyms

CQD Colloidal Quantum Dot. 34, *Glossary*: Colloidal Quantum Dot

EDO Experimental Data Object. 34

GUI Graphical User Interface. 11–14, 34

LED light-emitting diode. 3, 34

LNE Laboratory for Nanoelectronics. 11, 22, 34

NC nanocrystal. 1, 3, 5, 6, 34

PbS lead sulfide. 22, 34

PL photoluminescence. 1, 22, 23, 25, 34

QD Quantum Dot. 1–3, 6, 11, 22–25, 34, 35

QDO Quantum Dot Object. 12, 14, 16, 34

QDOA Quantum Dot Object Array. 14, 16, 34

QDOG Generic Quantum Dot Object. 34

TEM Transmission electron microscopy. 22, 24, 34, *Glossary*: Transmission electron microscopy

TOM Toolbox for OMEN in MATLAB. 11, 12, 17, 34

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Declaration of Originality

We hereby declare that the written work we have submitted entitled

Simulation of Quantum Dots

is original work which we alone have authored and which is written in our own words.

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