Computational modeling and analysis of quantum dots

Lam, Ah Wah

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**NANYANG
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**COMPUTATIONAL MODELING AND ANALYSIS
OF QUANTUM DOTS**

LAM AH WAH

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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Computational Modeling and Analysis of Quantum Dots

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School of Mechanical and Aerospace Engineering

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List of Abbreviation and Symbols

0D	Zero-Dimension
1D	One-Dimension
2D	Two-Dimension
2DEG	Two-Dimension Electron Gas
3D	Three-Dimension
Å	Angstrom
AFM	Atomic Force Microscopy
Au	Gold
CdS	Cadmium Sulphide
CdSe	Cadmium Selenide
CL	Capping Layer
DFT	Density Functional Theory
DOS	Density of States
E	total energy
EMA	Effective Mass Approximation
EPM	Empirical Psuedopotential Method
exciton	bound pair of conduction band electron and valence band holes
eV	electron volt
FCC	face centered cubic
FEM	Finite Element Method
FWEMA	Finite Well EMA
GaAs	Gallium Arsenide
$g(E)$	Energy density function
Ge	Germanium

H	Hamiltonian
HF	Hartree-Fock
ICL	Interfacial Capping Layer
InAs	Indium Arsenide
InP	Indium Phosphate
L	Momentum quantum number
LDA	Local Density Approximation
MBE	Molecular Beam Epitaxy
meV	milli-electron volt
MOCVD	Metal Organic Chemical Vapor Deposition
MOVPE	Metal Organic Vapor Phase Epitaxy
nm	nanometer
ns	nanosecond
PL	Photoluminescence
PbTe	Lead Telluride
QD	Quantum Dot
QR	Quantum Ring
QCE	Quantum Confinement Effect
QSE	Quantum Size Effect
qubits	Quantum bits
QWR	Quantum Wire
QW	Quantum Well
S	Spin quantum number
SAQD	Self-Assembled Quantum Dot
SK-growth	Stranski-Krastonov growth
Si	Silicon
SJ	Simple Jellium
TEM	Transmission electron microscope
UJ	Ultimate Jellium
UV	Ultraviolet
VFF	Valence Force Field

WL	Wetting Layer
α, a_T	thermal expansion coefficient
a_B^*	bulk effective Bohr radius
a_c	Conduction band deformation potential under hydrostatic deformation
a_{ex}	exciton radius
a_h	Valence band deformation potential under hydrostatic deformation
a_o	Lattice constant
β_{isj}	bond bending force constants
c	Speed of light in free space
δ_x	partial differentiate $\frac{\partial}{\partial x}$
d	Diameter
$d_{electronic}$	Electronic diameter
d_{ij}	Equilibrium distance between indexed objects
$D_{ij}^{\alpha\beta}$	Deformation potential tensor
ϵ_h	Hydrostatic strain
ϵ_b	Biaxial strain
$\epsilon_{ij}, e_{ij}, \epsilon_{\alpha\beta}$	Strain tensor
E	Young modulus
E	Energy
E_{AE}	Atomistic elasticity
E_{CE}	Continuum elasticity
E_e	Electron energy
E_h	Hole energy
E_{hh}	Heavy hole energy
E_{lh}	Light hole energy
ε_i, E_n	Eigenenergies
E_f	Fermi energy
E_g or E_{gap}	Band gap energy
ΔE_g	Band gap shift or transition energy, $E_g - E_g^{bulk}$
E_g^{bulk}	Energy band gap of bulk material
E_{Ry^*}	Rydberg's energy

ϵ_o	Permittivity of free space
ϵ, ϵ_r	Engineering relative permittivity
ϵ_T	Thermal strain
F_i	Body forces
g^*	Zeeman coupling
$\hbar$	Planck's constant/ 2π
$\hat{H}$	Hamiltonian
h	Height
H_a^*	Hartree constant
$\hat{H}$	Hamiltonian operator
H_k	Kinetic Hamiltonian
H_s	Strain Hamiltonian
∇^2	Laplacian operator
λ	Wavelength or Lamé constant, according to context
λ_i	Eigenvalues
L	Width
m	Mass
m_e	Mass of electron
m_e^*	Effective mass of electron
m_h	Mass of hole
m_h^*	Effective mass of hole
μ	Reduced mass or Lamé constant, according to context
M	Translational mass
ν	Poisson ratio or spectral frequency, according to context
n_x	Quantum number in x-dimension
n_y	Quantum number in y-dimension
N	Number of atoms
N_{cell}	Number of atoms in unit/basic lattice cell
Ψ	Quantum mechanical wave function
$\phi(r), \psi(r)$	Envelope wave function
$ \phi(r) ^2$	Probability density function

$ \psi(r) ^2$	Probability density function
r	Position vector
r_{ij}	Position vector between indexed objects
r_s	Electron density parameter
R	Radius
R_{eff}	Effective radius
Θ_{ijk}	Bond angle
T	Temperature
ΔT	Change of the temperature
u_i	Displacements
U_{KVFF}	Keating's strain energy
V	Potential or volume, according to context
$V^{\alpha\beta}(r)$	Strained-induced potential
V_o	External potential or physical volume, according to context
V_{eff}	Effective volume
V_c	Conduction band offset of electron
V_{hh}	Valence band of heavy hole
V_{lh}	Valence band of light hole
$V_{\text{electronic}}$	Electronic volume
V_t	Volume of shell layer
$V(r)$	Potential in radial dimension
$V(x)$	Potential in x-dimension
$V(x, y)$	Potential in x- and y-dimensions
V_e	Confinement potential of electrons
V_h	Confinement potential of holes
V_{SO}	Spin-orbit coupling
V_{strain}	Strained-induced potential

Summary

This PhD thesis documents the research carried out on the computational modeling and analysis of quantum dots. The main objectives are to model the electronic structure of the colloidal and self assembled quantum dots, and to quantify the quantum size effect (QSE) with respect to size, shape and material compositions.

The various computational models such as effective mass approximation (EMA), finite width effective mass approximation (FWEMA), and finite element method (FEM) were explored. The FEM was found to be suitable for the numerical analysis of the transition energies of the electron and hole, and the stresses and strains in the quantum dots.

In this work, two types of quantum dots are modeled, namely: self-assembled quantum dots and colloidal quantum dots. The structural properties such as strain and the strain-modified potential of the indium arsenide/gallium arsenide (InAs/GaAs) self-assembled quantum dots (SAQD) were obtained using the FEM and the **k.p** method. The electronic properties of the gold (Au), indium phosphate (InP), cadmium sulphide (CdS), zinc oxide (ZnO), copper chloride (CuCl), cadmium selenide (CdSe) colloidal quantum dots and indium arsenide/gallium arsenide (InAs/GaAs) self assembled quantum dots were studied by solving the single-particle EMA Schrödinger equation using the FEM.

Subsequently, several energy-size models were developed to evaluate the quantum size effects, such as:

1. **core-shell model** where
$$\Delta E_g = E_f \left(1 - 3 \left(\frac{N_{cell}}{a_o^3} \right)^{1/3} t N^{-1/3} + 3 \left(\frac{N_{cell}}{a_o^3} \right)^{2/3} t^2 N^{-2/3} - \left(\frac{N_{cell}}{a_o^3} \right)^{3/3} t^3 N^{-1} \right),$$
2. **basic electronic volume model** where
$$\Delta E_g = E_f / \left(\frac{N_{cell}}{a_o^3} V_o \right)^\beta,$$
3. **electronic volume ($V_o - V_t$) model** where
$$\Delta E_g = E_f / (V_o - V_t),$$
4. **effective volume model V_{eff}** where
$$\Delta E_g = -E_{R_y^*} + 2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)/(3\mu^2e^2)V_{eff}$$

The effective volume model successfully depicts the exciton radius, a_{ex} , from small size to the bulk effective exciton Bohr radius, a_B^* , for colloidal quantum dots and self-assembled quantum dots of all shapes, sizes and material compositions.

The effective volume equation can be simply used to determine the exciton size with measured or calculated emission energy using

$$a_{\text{ex}} = R_{\text{eff}} = \left(\frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{(3\mu^2e^2)} / \frac{4\pi}{3} (\Delta E_g + E_{R_y^*}) \right)^{1/3}$$

and effective volume can be rewritten as

$$\Delta E_g = -E_{R_y^*} + \frac{4}{3\pi} \left[\frac{\hbar^2\epsilon}{\mu e^2} \right] \left(\frac{\hbar^2\pi^2}{2\mu} \frac{1}{\frac{4\pi}{3} a_{\text{ex}}^3} \right) = -E_{R_y^*} + \frac{1}{\pi^2} [a_B^*] \left(\frac{\hbar^2\pi^2}{2\mu} \frac{1}{a_{\text{ex}}^3} \right)$$

where we can see that the ΔE_g is dependent on the ratio, a_B^*/a_{ex}^3 .

Chapter 1

Introduction

Quantum dots are small structures with typical sizes ranging from several nanometers to a few microns. In semiconductors all electrons are tightly bound to the nuclei except for a small fraction of free electrons. This small number can be a single free electron to several thousands in quantum dots. The nanostructure confines the motion of conduction band electrons and valence band holes in three spatial directions. The spatial confinement of charge carriers within nanometric dimension leads to a systematic transformation of their energy spectra from a set of continuum to a set of discrete states. This phenomenon is called the quantum size effect. The transformation sets in when the size of the particle becomes comparable to the exciton Bohr radius. A quantum dot has a discrete quantized energy spectrum, where size, shape and material properties affect the energies. The complete quantum confinement of electrons and holes in nanoscale structures results in a discrete energy spectrum of charge carriers similar to the energy levels seen in atoms. There exist electron shells fulfilling the Hund's rules and the quantum dot has thus been sometimes termed the **artificial atom**. The resulting spectral properties of quantum dots are unique and may be exploited in a wide variety of applications, including laser emitters, optical memory structures, single electron transistors, field-effect transistors, charge storage devices and quantum computers.

The research on quantum dots date back to the 1960's where the influence of micron-size crystal on the spectral response limit was reported by Lawson et al. [1960]. In that work, photoconductive layers of lead telluride (PbTe) were formed by evaporation on substrates at different temperature and a correspondence was obtained between crystal size and limit of spectral response [Wood and Ashcroft, 1982].

Following a lull, and next phase of development occurred in the early 1980's when Ekimov and Onushchenko [1982] detailed the quantum size effect in three-dimensional microscopic semiconductor crystals; Rossetti and Brus [1982], Rossetti

et al. [1983, 1984] worked on electron-hole recombination emission as a probe of surface chemistry in aqueous CdS colloids, on quantum size effects in the redox potentials, resonance Raman spectra, electronic spectra of CdS crystallites in aqueous solution, and on electron-hole recombination emission of aqueous CdS colloids and size effects in the excited electronic states of small colloidal CdS crystallites; Brus [1983, 1984a] developed a simple model for ionization potential, electron affinity, and aqueous redox potentials of small semiconductor crystallites, and examined electron-electron and electron-hole interactions in small semiconductor crystallites and the size dependence of the lowest excited electronic state; and Knight et al. [1984] investigated electronic shell structure and abundances of sodium clusters.

The acceleration of semiconductor technologies from the 1970's such as molecular beam epitaxy (MBE) and measuring instruments such as atomic force microscopy (AFM) led to the creation of self-assembled quantum dots (SAQD) in the 1980's. Reed et al. [1988] observed discrete electronic states in the zero-dimensional semiconductor nanostructure.

In 1996, an experimental breakthrough occurred when Tarucha et al. [1996] reported shell filling and spin effects in a few electron quantum dots using the 2D electron gas (2DEG) semiconductor device setup. They were the first to demonstrate very clearly the electronic shell structure of small vertical dots. The existence of electron shell fulfilling the Hund's rules was unambiguously confirmed with a one-by-one charging of single electrons. Since the early 1990's, the quantum dot has been termed artificial atom [Meurer et al., 1992, Kastner, 1993, Reed, 1993, Ashoori, 1996].

The density of states (DOS) for bulk material, quantum well (QW) with 2-dimensional (2D) confinement, quantum wire (QWR) with 1-dimensional (1D) confinement and quantum dot (QD) with 0-dimensional (0D) confinement are depicted in Figure 1.1.

Figure 1.1: Bulk material and confinements for quantum well (QW), quantum wire (QWR) and quantum dot (QD) - Evolution of the density of states as the dimensionality of the structure is reduced from 3D (bulk) to 0D (quantum dot). The density of states of an ideal quantum dot is discrete, like in an atom. Quantum wires, which confine the motion of electrons and holes in two spatial directions and allow free propagation in the third. Quantum wells, which confine the motion of electrons and holes in one direction and allow free propagation in two directions. Quantum dots confined the electrons and holes in all three directions. As the dimensionality of the structure reduce Density of State (DOS), $g(E)$ becomes sharper and pronouncedly discrete. (Image Source: Maranganti and Sharma [2005])

1.1 Quantum dots

There is no strict distinction in literature between the terms clusters, nanoclusters, nanoparticles, nanocrystals and quantum dots. However, “clusters” are often used for agglomerates of very few atoms, “nanoparticles” for larger agglomerates (usually of metals or carbon), and “quantum dots” for semiconductor particles and islands.

Quantum dots are zero-dimensional (0D) nanometer-sized, usually man-made structures, where a few or up to several thousands electrons are confined [Reed et al., 1988]. A quantum dot contains a small finite number (of the order of 1-100) of conduction band electrons, valence band holes, or excitons, i.e., a finite number of elementary electric charges as illustrated in Figure 1.2 where the energies are quantized.

Figure 1.2: 3D-Confinement of charge carriers of a lens-shaped self-assembled quantum dot with wetting layer. The diagram shows the discrete energy levels at the electron-band and valence-band, and the density wave functions for the s-, p- and d-shells. (Image Source: IEF, <http://pages.ief.u-psud.fr/QDgroup/modeling.html>)

Quantum dots are interesting objects. As highly correlated many-particle systems with tunable properties, they are excellent for studies of electron-electron interactions. The spin effects are also pronounced in quantum dots. The magnetic field needed to produce spin effects of similar magnitude in atoms is millions of times higher than in quantum dots. For small quantum dots complete spin polarization can be easily achieved in laboratories. Quantum dots can be manufactured in a number of different ways. Vast quantum dot arrays can be created using self-assembly methods or by cluster deposition. Both metallic and semiconductor dot arrays can be made.

There are three usual methods to artificially create quantum dots:

1. Confinement of two-dimensional electron gas (2DEG) as illustrated in Figure 1.3;

2. Wet chemistry methods [Guyot-Sionnest, 2008] to create spherical/spheroidal colloidal quantum dots or nanoclusters (sometime also called nanocrystals) as illustrated in Figure 1.4;
3. Stranski-Krastanov (SK) growth by molecular beam epitaxy (MBE) [Franchi et al., 2003] to create self-assembled quantum dots (SAQD) of pyramidal/truncated-pyramidal or lens/cone-shaped quantum dots with the MBE setup in Figure 1.5 .

Figure 1.3: Schematic representation of the 2DEG devices. (a) Heterostructure in a vertical cross section. Thickness of the layers: cap 24 nm, donor layer 36 nm, spacer 10 nm. The substrate is assumed to have an infinite thickness. The 2DEG is localized near the interface between the substrate and the spacer under the influence of the applied voltage V_g between the gate and the substrate. (b) Symmetric square quantum dot. The size of the gate opening is $R=110$ nm. (c) Asymmetric square quantum dot. The gate geometry is the same as in (b) except for the cut corner of the width $W=20$ nm and variable length, from $L=0$ nm (symmetric square dot) to $L=110$ nm (rectangular dot). (d) Two coupled square quantum dots. The gate openings are squares of $R=110$ nm; the interdot distance is varied from $d=0$ to $d=200$ nm. (Image Source: Yakimenko et al. [2001])

Figure 1.4: Chemical synthesis to obtain colloidal quantum dots with different colors. (Image Source: Klimov [2003])

Figure 1.5: Growth of self-assembled quantum dot by MBE. (Image Source: Wikipedia, <http://en.wikipedia.org>)

Small quantum dots, such as colloidal semiconductor nanocrystals, can be as small as 2 to 10 nm, corresponding to 10 to 50 atoms in diameter and a total of 100 to 100,000 atoms within the quantum dot volume. Self-assembled quantum dots are typically between 10 and 50 nm in size. Quantum dots defined by lithographically patterned gate electrodes, or by etching on two-dimensional electron gases in semiconductor heterostructures can have lateral dimensions exceeding 100

nm. At 10 nm in diameter, nearly 3 million quantum dots can be lined up end to end and fit within the width of a human thumb.

Quantum dots can also be compared to atoms: both have a discrete energy spectrum and bind a small number of electrons. In contrast to atoms, the confinement potential in quantum dots does not necessarily show spherical symmetry. In addition, the confined electrons do not move in free space, but in the host crystal. The quantum dot host material, in particular its band structure therefore plays an important role for all quantum dot properties. Typical energy scales, for example, are of the order of ten electron volts in atoms but only 1 millielectron volt (meV) in quantum dots. Quantum dots with a nearly spherical symmetry, or flat quantum dots with nearly cylindrical symmetry can exhibit shell filling according to the equivalent of Hund's rules for atoms. Such dots are sometimes called "artificial atoms". In contrast to atoms, the energy spectrum of a quantum dot can be engineered by controlling the geometrical size, shape, and the strength of the confinement potential. Also, in contrast to atoms, it is relatively easy to connect quantum dots by tunnel barriers to conducting leads, which allows the application of the techniques of tunneling spectroscopy for their investigation.

As in atoms, the energy levels of small quantum dots can be probed by optical spectroscopy techniques. In quantum dots that confine electrons and holes, the interband absorption edge is blue shifted due to the confinement compared to the bulk material of the host semiconductor material. As a consequence quantum dots of the same material but with different sizes can emit light of different colors.

Quantum dots are particularly significant for optical applications due to their theoretically high quantum yield. In electronic applications they have been proven to operate like a single-electron transistor and display the Coulomb blockade effect. Quantum dots have also been suggested as implementations of qubits for quantum information processing.

One of the optical features of small excitonic quantum dots immediately noticeable to the unaided eye is coloration. While the material which makes up a quantum dot defines its intrinsic energy signature, more significant in terms of coloration is the size. The larger the dot, the redder (the more towards the red end of the spectrum) the fluorescence. The smaller the dot, the bluer (the more towards the blue end) it is. The coloration is directly related to the energy levels of the quantum dot. Quantitatively speaking, the band gap energy that determines the energy (and hence color) of the fluoresced light is inversely proportional to the square of the size of the quantum dot. Larger quantum dots have more energy levels which are more closely spaced. This allows the quantum dot to absorb photons containing less energy, i.e. those closer to the red end of the spectrum. Recent literature suggests

that the shape of the quantum dot may well also be a factor in the colorization, but as yet not enough information is available.

1.1.1 Two-dimensional electron gas (2DEG)

The 2DEG quantum dots are fabricated by restricting the two-dimensional (2D) electron gas in a semiconductor heterostructure laterally by tiny electrostatic gates or vertically by etching techniques. One can control the confinement, the electron number and thus the density and the interaction strength. This is the major advantage over other methods and it allows fundamental physics to be explored. The structure of the 2DEG device of the GaAs/AlGaAs heterostructure and band diagram are shown at Figure 1.6.

The nanoscale structures are able to capture and localize charge carriers, such as electrons. Typical dimensions for quantum dots range from nm to a few micrometers, and the number of electrons can be tuned from zero to up to the thousands. Quantum dots resemble ordinary atoms in many ways. Both contain a more or less fixed number of electrons, have a shell structure, and even the experimental Hund's rule describing the spin alignment in atomic shells holds for quantum dots in many cases. These similarities gave rise to the term artificial atom, which is commonly used as a synonym for the quantum dot.

Quantum dots can be manufactured at semiconductor interfaces, which have a quasi-two-dimensional electron gas (2DEG) in the inversion layer. Electrodes, which create the confining electrostatic potential and contacts to the dot, can be made with lithographic techniques on top of the structure, thereby producing lateral dots. By etching away most of the 2DEG interface, vertical semiconductor dots can be created. Vertical dots are typically smaller than lateral dots, down to the size of a single-electron dot.

Figure 1.6: The structure of the 2DEG device, the GaAs/AlGaAs heterostructure and band diagram. The GaAs/AlGaAs heterostructure is comprised of a bulk GaAs substrate, a layer ($\sim 50\text{-}200$ nm thick) of $\text{Al}_x\text{Ga}_{1-x}\text{As}$, and a plain GaAs cap (~ 10 nm). The AlGaAs layer is partially doped with n-type donors which contribute electrons to a two dimensional electron gas (2DEG) that forms at the interface at low temperature. Gold (Au) gates and Ni-Au-Ge ohmic contacts are patterned on the surface during device fabrication. The ohmic contacts are annealed so that their metal diffuses down and makes electrical contact with the 2DEG. The band diagram of the GaAs/AlGaAs wafer is shown on the right with energy on the horizontal axis. At low temperature, electrons fill the triangular potential well at the GaAs/AlGaAs interface up to the Fermi energy, forming the 2DEG. (Image Source: Wikipedia, <http://en.wikipedia.org>)

1.1.2 Colloidal quantum dot

The colloidal quantum dots were schematically studied in the 1960's [Zheng et al., 2004, Fonoberov and Pokatilov, 2002, Joswig et al., 2000, Li and Wang, 2005, Rossetti et al., 1984, Marin et al., 1998, Brus, 1984a, Murray et al., 1993]. One of the main issues in quantum dot research is to investigate the dependencies of the intrinsic properties to the sizes of the quantum dots. Besides the change in size, the change in shape also leads to different electronic states and energy band gaps in nanocrystals. With rapid developments in chemical synthesis [Narayanan and Pal, 2006, Mercier et al., 2007, Guzelian et al., 1996, Murray et al., 2001], the control of nanocrystal size, shape, and dimensionality have become possible as illustrated in

Figure 1.7 and Figure 1.8.

Figure 1.7: Fluorescence of colloidal QD of various sizes displaying colors. They are used for labeling in biological investigations. (Image Source: Wikipedia, <http://en.wikivisual.com>)

Figure 1.8: The emission light frequency for various sizes of CdS colloidal nanocrystals quantum dot. The diameter or size of the nanocrystal is directly related its UV curve peak position. Its diameter will determine its absorbance and emission properties. (Image Source: Wikipedia, <http://en.wikipedia.org>)

1.1.3 Self-assembled quantum dot

Self-assembled quantum dots have been extensively studied since the 1980's [Pryor, 1998, Stier et al., 1999, Wang et al., 2000b, Stoleru et al., 2002, Melnik and Willatzen, 2004] when atomic layer-to-layer growth became possible. The growth of

self-assembled quantum dots based on Stranski-Krastanov growth mode is shown in Figure 1.9.

Figure 1.9: SAQD Growth Modes. The growth of self-assembled quantum dots are based on Stranski-Krastanov growth mode. The wetting layer assists in the nucleation of quantum dot. (Image Source: Wikipedia, <http://en.wikipedia.org>)

The strains inside and around the quantum dot influence the electronic and optical properties of the quantum dot system. Many methods of modeling quantum dot systems have been developed to analyze the stress and strain fields. The first category is the analytical continuum approach based on Eshelby's inclusion theory [Eshelby, 1957]. This approach treats quantum dots as inclusions in an infinite matrix, and elastic isotropy and uniformity of elastic properties in both quantum dots and the matrix are assumed. The second method is the atomistic approach. A common technique of this approach is the valence force field (VFF) model with the Keating potential [Keating, 1966]. The third category is the numerical approach based on continuum elasticity. This basically utilizes the finite difference and the finite element method (FEM) whereby the strain energy of the structure is minimized.

The mechanical behavior plays a role because the available electron energy levels, which depend on the underlying electronic structure of the crystalline material, are sensitive to strain. Strain plays a key role in the formation of quantum dots and in determining their electronic and optoelectronic properties. Lattice distortion in and around buried quantum dots is responsible for piezoelectric fields and for a significant modification of the band structure. The calculation of the strain distribution is an

essential precursor to calculations of the optical properties of devices, where efficient and accurate methods of calculating strain are required, for a range of geometries, for quantum dot arrays and for quantum dots exhibiting composition variation.

It has been reported that a 1% change in strain of the quantum dot results in ~ 20 meV order changes in the electronic structure. Such changes are observable in the photoluminescence (PL) spectrum.

Self-assembled quantum dots nucleate spontaneously under certain conditions during molecular beam epitaxy (MBE) [Joyce et al., 2000], metal organic vapor phase epitaxy (MOVPE) [Richter, 2002] and metal organic chemical vapor deposition (MOCVD), when a material is grown on a substrate to which it is not lattice matched. The resulting strain produces coherently strained islands on top of a two-dimensional “wetting-layer” [Goldstein et al., 1985]. This growth mode is known as Stranski-Krastanov growth. The islands can be subsequently buried to form the quantum dot. This fabrication method has potential for applications in quantum cryptography (i.e. single photon sources) and quantum computation. The main limitations of this method are the cost of fabrication and the lack of control over positioning of individual dots. Please see Figure 1.10 where the Germanium, Ge, quantum dots are seemingly randomly distributed.

scanning tunneling micrograph

$1\ \mu\text{m} \times 1\ \mu\text{m}$

Liu et al, J. Vac. Sci. Technol. B 20, 678 (2002)

Pyramidal islands

Widths of 30 - 45 nm

Density is 2×10^{10} per cm^2

Sides slanted at 11.5°

Onset after 3 - 4 monolayers Ge deposited

Figure 1.10: Germanium, Ge, growth islands on Silicon, Si(001). (Image Source: Liu et al. [2002])

Depending on synthesis methods and conditions, the quantum dot can have a different size, shape, and alloy profile. A major task of the current research is to study the dependence of the electronic structure on the size, shape, and alloy profile.

A closed-up picture of the self-assembled pyramidal-shaped quantum dot is given in Figure 1.11.

Nanostructure of quantum dot

Figure 1.11: Self-assembled QD. A pyramidal-shaped quantum dot oriented in the 100-direction. The quantum dot contains from thousands to millions of atoms. (Image Source: Medeiros-Ribeiro et al. [1999])

1.2 Quantum dot applications

From the technological point of view [Maranganti and Sharma, 2005] the most important difference between quantum dots and atoms is that the properties of quantum dots can be tailored by design, even in real time, by adjusting the electromagnetic environment of the dot. This opens a broad spectrum of new possibilities ranging from superior laser technology to applications of quantum-dot transistor or memory technologies and even future applications in quantum computing [Loss and DiVincenzo, 1998, Bimberg, 2005].

It is possible to make the self-organized dots in the arrays extremely small, but the height of the dots is typically of the same order as their diameter, which makes them three-dimensional.

During the past 30 years, various nanocrystals have been synthesized and it has been found that their electrical and optical properties are dramatically different from their bulk counterparts. These small colloidal nanocrystals as promising advanced functional materials can be found in many different applications, ranging from lasers, solar cells, to single-electron transistors. One example of these nanocrystal applications is to incorporate them into biological systems as illustrated in Figure 1.12 and Figure 1.13. Cadmium selenide quantum dots permit *in vivo* cancer cell targeting and imaging in living mice. Many of these applications

are related to the size-dependence of the nanocrystal optical properties. In a semiconductor, the optical properties are related to the edge transitions of the electronic band gaps. Thus, studying the size dependence of the electron band gap and the related exciton energy is one of the most important topics in semiconductor nanocrystal research.

Figure 1.12: Multi-color immunofluorescence with colloidal quantum dot. (Image Source: Wikipedia, <http://en.wikipedia.org>)

Figure 1.13: The tagging of cells with orange-colored colloidal QD. (Image Source: Wikipedia, <http://en.wikipedia.org>)

Semiconductor quantum dot structures with atomic-like states are an area of intense investigation because this feature is expected to lead to improved optoelectronic devices such as quantum dot diode lasers which have narrow line-width and high modulation bandwidth because of the high differential gain and low threshold current density [Mirin et al., 1995].

Figure 1.14: Researchers at Los Alamos National Laboratory have developed a wireless nanodevice that efficiently produces visible light, through energy transfer from nano-thin layers of quantum wells to nanocrystals above the nanolayers. (Image Source: Los Alamos National Laboratory, <http://www.lanl.gov/worldview/news/photos/achermann7RED.jpg>)

Researchers at Los Alamos National Laboratory have developed a wireless nanodevice that efficiently produces visible light, through energy transfer from nano-thin layers of quantum wells to nanocrystals above the nanolayers, see Figure 1.14.

Being zero dimensional, quantum dots have sharper density of states than higher-dimensional structures. As a result, they have superior transport and optical properties, and are being researched for use in diode lasers, amplifiers, and biological

sensors.

Quantum dot technology is one of the most promising candidates for use in solid-state quantum computation. By applying small voltages to the leads one can control the flow of electrons through the quantum dot and thereby make precise measurements of the spin and other properties therein.

In June 2006, QD Vision, a leader in the development of next-generation displays, announced technical success in making a proof of concept quantum dot display. Quantum dots are valued for displays, because they emit light in very specific gaussian distributions. This can result in a display that can more accurately reflect the colors that the human eye can perceive. Quantum dots also require very little power since they are not color filtered. A LCD display, for example, is powered by a single fluorescent lamp that is color filtered to produce red, green, and blue pixels. Thus, when a LCD display shows a fully white screen, two-thirds of the light is absorbed by the filters. Displays that intrinsically produce monochromatic light can for this reason be more efficient, since more of the light produced reaches the eye.

1.3 Structural modeling of self-assembled quantum dots

The fundamental issues in self-assembled quantum dots (SAQD) are the epitaxy, structural, optical and transport properties. We are interested in the structural properties that encompass the strain tensor in the relaxed quantum dot and the electronic structure of the quantum dot due to the strain-induced potential.

The two practical approaches to model the strain are the classical continuum elasticity and atomic elasticity. The ab-initio methods such as Hartree-Fock (HF) and density functional theory (DFT) are only practical up to about 1,000's atoms. For the electronic structure, the **k.p** method or the atomistic pseudopotential method can be used.

1.3.1 Mechanical strains

The three approaches to calculate strains are the harmonic continuum elasticity, atomic elasticity, and the atomistic quantum-mechanical approach [Pryor et al., 1998].

Harmonic continuum elasticity

Here, one uses the classical elasticity within the harmonic approximation. For a cubic system, the strain energy per atom, E_{CE} , is

$$E_{CE} = \frac{V}{2}C_{11}(\epsilon_{xx}^2 + \epsilon_{yy}^2 + \epsilon_{zz}^2) + \frac{V}{2}C_{44}(\epsilon_{yz}^2 + \epsilon_{zx}^2 + \epsilon_{xy}^2) + VC_{12}(\epsilon_{yy}\epsilon_{zz} + \epsilon_{zz}\epsilon_{xx} + \epsilon_{xx}\epsilon_{yy}) \quad (1.1)$$

where V is the equilibrium volume, C_{ij} the cubic elastic constants, and $\epsilon_{\alpha\beta}$ the strain tensor.

The harmonic continuum elasticity method has been applied to pyramidal quantum dots by Grundmann et al. [1995].

Atomistic elasticity

In atomistic elasticity, the strain energy is described in terms of few body potentials between actual atoms,

$$E_{AE} = \sum_{ij} V_2(R_i - R_j) + \sum_{ijk} V_3(\Theta_{ijk}) + \dots \quad (1.2)$$

where V_2 is a two-body potential term, and V_3 is a three-body function of the bond angle, Θ_{ijk} .

The functional form of these terms is taken to be strain-independent. The strain is determined by minimizing E_{AE} with respect to atomic positions. Like the continuum elasticity approach, only the cubic elastic constants are used as input. However, unlike the continuum elasticity approach, here (a) optical phonon modes can be described, (b) harmonicity is not assumed, and (c) the atomic level symmetry is retained.

For a regular pyramid quantum dot, in the continuum representation, the strain is equal on the $\{110\}$ and $\{\bar{1}10\}$ facets, while in an atomistic description these two facets can have different strain if the pyramid is made of zincblende material. Atomistic elasticity has been widely used to determine strain in alloys, superlattices and dots, where V_2 and V_3 are taken from the Keating's valence force field (VFF) model.

Atomistic quantum-mechanical approach

In the ab-initio approach, one does not have to assume any model for interatomic interactions as in the atomic elasticity. Instead, one explicitly computes the total electron and nuclear energy $E_{tot}[\{R_i\}]$ for each atomic configuration $\{R_i\}$ directly

from the quantum mechanical Schrödinger equation. The atomic symmetry is retained and harmonicity is not assumed. This approach has been used for small (~ 100 atom) clusters but it is impractical for $\sim 100\text{\AA}$ quantum dots ($\sim 10^5$ atoms).

1.3.2 Mathematical model of quantum dots based on continuum elasticity

The continuum methods for calculating the strain distribution due to a uniformly lattice-mismatched inclusion were pioneered by Eshelby [1957]. The surge of interest in quantum dots has lead to a range of applications of his seminal work. For example, a set of vectors has been identified such that the divergence of each vector results in the Green's function for the stress component σ_{ij} . Gauss' theorem then enables the stress to be determined by performing an integral over the quantum dot space.

The mathematical model of a quantum dot based on continuum elastic theory is given as

$$\mu \nabla^2 u_i + (\lambda + \mu) \frac{\delta e_\nu}{\delta x_i} - (3\lambda + 2\mu) \frac{\Delta T}{\delta x_i} + F_i = 0 \quad (1.3)$$

and the boundary conditions are

$$\sigma_{ni}(3\lambda + 2\mu)\alpha(\Delta T)l_i = \mu \left(\frac{\delta u_i}{\delta x_j} \right) l_j + \lambda l_i e_\nu \quad (1.4)$$

where u_i stands for displacements, $i, j=1,2,3$ (or x, y, z in the case of Cartesian coordinates), ΔT is the change of the body temperature relative to the arbitrary reference temperature, F_i are the body forces, n_i the normal components of the stress vector, $e_\nu = e_{11} + e_{22} + e_{33}$ the volumetric strain, α the thermal expansion coefficient, λ and μ the Lamé constants (which can be expressed in the terms of Young modulus, E), and ν the Poissons ratio.

The initial temperature can be taken as reference. The quantum dot region is heated without heat transfer or we can equivalently assume zero-expansion coefficient at the matrix region. The final temperature of the quantum dot is chosen such that its lattice constant would reach that of the actual quantum dot if not immersed into the matrix material. Using this equivalent approach with additional boundary conditions to maintain the quantum dot form, the same strain field can be obtained. By solving the differential equation for displacement, all relative quantities can be obtained, particularly the six independent strain tensor components, $e_{ij}(x, y, z)$,

$$\begin{aligned}
e_{11} &= \frac{\delta u_1}{\delta x_1} \\
e_{22} &= \frac{\delta u_2}{\delta x_2} \\
e_{33} &= \frac{\delta u_3}{\delta x_3} \\
e_{12} = e_{21} &= \frac{1}{2} \left(\frac{\delta u_2}{\delta x_1} + \frac{\delta u_1}{\delta x_2} \right) \\
e_{13} = e_{31} &= \frac{1}{2} \left(\frac{\delta u_3}{\delta x_1} + \frac{\delta u_1}{\delta x_3} \right) \\
e_{23} = e_{32} &= \frac{1}{2} \left(\frac{\delta u_3}{\delta x_2} + \frac{\delta u_2}{\delta x_3} \right)
\end{aligned} \tag{1.5}$$

We need to know the Young modulus, E , the Poisson ratio, ν , and the thermal expansion coefficient, α , in order to numerically solve the differential equations.

Other similar continuum methodologies were reported by [Voon and Willatzen, 2002, Pearson and Faux, 2000] for self-assembled quantum dots.

1.3.3 Atomic elasticity with Keating valence force field

The valence force field (VFF) model is a hybrid molecular mechanics model. It can be used to model quantum dots to calculate accurate elastic constants and electronic structures of complex geometry of quantum dots within reasonable time. The starting point for almost all VFF models used is the form given by Keating (KVFF),

$$U_{\text{KVFF}} = \sum_{s=1}^N \left\{ \sum_{i=1}^N \left[\frac{3}{4d_{si}^2} \alpha_{si}^2 (r_{si} \cdot r_{si} - d_{si}^2) + \sum_{j=1, j \neq i}^4 \frac{3}{8d_{si}d_{sj}} \beta_{isj} (r_{si} \cdot r_{sj} - d_{si}d_{sj} \cos(\Theta_{isj}))^2 \right] \right\} \tag{1.6}$$

The strain energy U_{KVFF} is calculated by a summation over the N atoms of the unit cell. Only the next neighbors i, j of atoms are included in the interaction. Their actual distance vector is given by r_{ij} with its equilibrium length d_{ij} . The electronic part of the system is implicitly contained in the effective bond stretching parameter α_{si} , describing the two body interaction between the atoms s and i , and the bond bending force constants, β_{isj} , describing the three body interaction of atoms i, s, j which in equilibrium form a common angle Θ_{isj} , around atom s .

The advantage of the formulation by Keating is that the three unknown parameters d , α , and β can be easily derived from the corresponding bulk systems: d being the ideal bond length, α and β can be readily calculated from the elastic constants.

The KVFF has been enhanced by others to include the Coulomb interactions and polarization effects.

The main advantage of VFF models is the low computational cost compared with first principles calculations. A sufficient accuracy is possible by consistent determination of their parameters. Therefore the fitted KVFF is suitable for strain relaxation in large cells with more than 1,000 atoms and as tools for atomic pre-relaxation in first principles calculations.

1.4 Electronic structure of quantum dots

Electronic structure theory describes the motion of electrons in atoms or molecules [Kohn, 1999a,b, Leburton et al., 1999, Lyalin et al., 2000, Boxberg and Tulkki, 2007]. However, the first principle Schrödinger equation can only be analytically solved for the hydrogen atom (with one electron) and Helium atom (with two electron) as the electron-electron effect is complex.

The quantum mechanics is applicable to quantum dots. Generally this is done in the concept of Born-Oppenheimer approximation [Born and Oppenheimer, 1927] with separate motions of the electrons and nuclei. The central equation of the quantum mechanics is the Schrödinger equation. Quantum mechanics particles are described with wave functions Ψ which are solutions of the Schrödinger equation

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \quad (1.7)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ is a quantum mechanical wave function and $\hbar$ is the reduced Planck constant $h/2\pi$.

1.4.1 One-particle time-independent Schrödinger equation

Quantum dots have been modeled with one-particle time-independent Schrödinger equation eigenvalue problem and solve numerically

$$\hat{H}\Psi = E\Psi \quad (1.8)$$

where E is the total energy, and Ψ the wave function of all the particles. All the physical properties can be calculated from the wave function Ψ .

1.4.2 Major differences between hydrogen atom and quantum dot

There are two major differences between the hydrogen atom and a quantum dot. The difference in the order of levels between the hydrogen atom and the quantum dot is explained by the fact that in hydrogen atoms the Coulomb potential is deeply singular at $r = 0$, while there is no singularity in the quantum dot. The separation of the successive energy levels increases when the quantum number n increases, i.e. when we go up to the top of the dot confinement well. This feature is contrary to the case of a normal atom, in which the separation between energy levels of highly excited states becomes lower and lower when n increases.

1.4.3 Quantum dot Hamiltonian

Only a couple of electrons at time can be made free to move in the quantum dot region. Although an electron is effectively free to move, its motion is affected by the surrounding core/ionic/lattice material. We can describe electron motion in a quantum dot by substituting the mass of a free electron with the effective mass of the electrons (holes) of the host material in the Hamiltonian $m_{e,h} \rightarrow m_{e,h}^*$. This is called the effective mass approximation [Polimeni et al., 2004, Tablero, 2005, Lee et al., 2005, Li et al., 1996, Heidari et al., 2007].

The model quantum dot Hamiltonian of N electrons in a homogenous external magnetic field along z-axis ($B = Bu_z = \nabla \cdot A$) can be written as:

$$\hat{H} = \sum_i^N \left\{ \frac{(-\hbar \nabla_i + \frac{e}{c} A(r_i))^2}{2m^*} + V_e(r_i) + V_{SO}(r_i) + g^* \mu_B B \cdot S_i \right\} + \sum_{i < j}^N \frac{e^2}{\varepsilon |r_i - r_j|} \quad (1.9)$$

where the $A(r_i)$ kinetic term is due to magnetic field, the potential $V_e(r_i)$ describes the quantum dot confinement of electrons and $V_{SO}(r_i)$ the spin-orbit interaction, and the g^* term is the Zeeman coupling to the electron spin. The last term is the coulomb repulsion between electron pairs.

For the case of a single electron or hole, without external magnetic field, the Hamiltonian can be simplified as

$$\hat{H} = \nabla_{e,h}^2 + V_{e,h}(r) \quad (1.10)$$

1.4.4 Model confining potential, $V_e(r)$ and $V_h(r)$

Harmonic potential

The harmonic (parabolic) potential is a good approximation to the real potential and it is also convenient. Many of the physical phenomena observed in experiments have been reproduced within the harmonic approximation

$$V_{e,h}(r) = \frac{1}{2}m_{e,h}^*\omega_0^2r^2 \quad (1.11)$$

where $m_{e,h}^*$ is the effective mass of electron (hole) and ω_0 provides a measure of the strength of the confinement. The value of the confinement energy $\hbar\omega_0$ is typically in the few meV range.

Finite and infinite potential

The other commonly used confinement potentials are the infinite hard-wall potential and the finite hard-wall potential given in Equation(1.12) and Equation(1.13) respectively.

$$V_{e,h}(r) = \begin{cases} 0, & r \leq L/2 \\ \infty, & elsewhere \end{cases} \quad (1.12)$$

$$V_{e,h}(r) = \begin{cases} 0, & r \leq L/2 \\ V, & elsewhere \end{cases} \quad (1.13)$$

The confined wave functions $|\psi|$ for the finite square well (in arbitrary units) with width L of 1, 2 and 4 units and confinement potentials $V(r)$ of 2.5 and 10 units are shown in Figure 1.15. The energy levels are “quantized” and there are more energy levels for the deeper well with wider width. The “tails” of the wave functions $|\psi|$ penetrate into the barrier material.

Figure 1.15: The wave functions, ψ , confined in the 1D finite square well of width 1, 2, and 4 arbitrary units, in potential of 2.5 and 10 arbitrary units. There are more energy levels for the deeper well and wider width.

1.5 Objectives of this work

In this work, quantum dots will be researched with respect to the structural and electronic properties and particularly with respect to shift in energy with sizes at the nanoscale. The confinement of exciton and the exciton volume shall be the focus of our study. The objectives of this research are as follows:

1. Literature review and assessment of the historical development of quantum dots, and the quantum size effect models based on size, shapes and material types. We explore the computational models of quantum dots and carry out numerical simulation of the 2D-square quantum dots in infinite well and analyze the energy shells and Hund's rule for the artificial atom, the 3D pyramidal self-assembled quantum dots in finite well, and the 3D spherical colloidal quantum dots in finite well.
2. Examine the effects of interfacial capping layer (ICL) on the stresses and strains in the self-assembled InAs/GaAs pyramidal quantum dots using the finite element method (FEM), and the change in band gap energy due to the strain-induced potential using the one-band **k.p** method.
3. Model the electronic properties of colloidal and self-assembled quantum dots with the finite well effective mass approximation (FWEMA) and solve using the finite element method (FEM).
4. Develop quantum size effect models of the confined exciton (electron-hole quasi-particle) for quantum dots of different material types and shapes, and examine the exciton radii with physical size of the quantum dots.
5. Define the effective volume model and compare the effective volume with exciton volume for various sizes, shapes and materials.

1.6 Layout of the report

In this chapter, we give an introduction to quantum dots, the applications of quantum dots, and the modeling of the confined carriers (electron, hole, exciton quasi-particle) in quantum dot using the Schrödinger equation.

In chapter two, we explain the basic models and the carriers confinement in finite and harmonic wells. We provide a comprehensive analytical study of quantum confinements from the 1D finite confinement well to the 3D harmonic confinement, the finite element method (FEM), the FEM discretization of the Schrödinger quantum mechanical eigenvalue equation, the pseudopotential and the **k.p** method with strain potential calculation in continuum elasticity model.

In chapter three, we model and simulate the structural and electronic properties of “classic” 2D square quantum dots confined in an infinite well, the realistic 3D self-assembled pyramidal quantum dots and 3D colloidal quantum dots in a finite well. The electronic energies from our FEM simulation of a 2D square quantum well are presented and validated against the exact analytical method, and we demonstrated the energy shell structures similar to Hund’s rule. The results of the 3D pyramidal self-assembled quantum dots are validated with numerical finite volume method (FVM) data, and the 3D colloidal quantum dots with experimental data.

In chapter four, we simulate the structural strains in the 3D pyramidal InAs/GaAs self-assembled quantum dot with interfacial capping layer, $\sim 0.3\text{nm}$, with the usual wetting layer and capping layer. We introduce the new interfacial capping layer (ICL) and study the spatial variation of the stress and strain within the quantum dot, the wetting layer, interfacial capping layer and the surrounding matrix. The strain-induced confinement confinement was calculated using the one-band **k.p** method to obtain the band gap shift due to the strain.

In chapter five, we evaluate the size effect on band gap energies for gold (Au), indium phosphate (InP) and cadmium selenide (CdSe) colloidal quantum dots. We define the core-shell model to obtain the electronic volume, and compare it against the bulk effective exciton Bohr radius, a_B^* .

In chapter six, the $(V_o - V_t)$ volume model based on the generalized $\Delta E_g = a + b/(V_o - V_t)$ equation is introduced. Similarly we evaluate the electronic radius, $(V_o - V_t)^{1/3}/2$, and compare it against the bulk effective exciton Bohr radius, a_B^* .

In chapter seven, we refine the volume model using $\Delta E_g = a + b/V_{\text{eff}}$. The model is then applied to the CdS, ZnO, CuCl and CdSe colloidal quantum dots, and derive $a = -E_{R_y}^*$ and $b = 2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)/(3\mu^2e^2)$, which results in an excellent match to the bulk effective exciton Bohr radius, a_B^* . Thus, we conclude that effective radius, R_{eff} , depicts the exciton radius, a_{ex} .

In chapter eight, the generalized effective volume model that is applicable to all practical shapes of quantum dots is developed. This model is then applied to different shapes such as pyramid, dome, hourglass, cylinder, etc. The effective volume model was found to be applicable to all regular and hypothetical shapes of quantum dots.

We conclude the present work, and propose the future works in chapter nine. We also summarize our findings and the analysis of the quantum dots with respect to the confinement energies and volume models.

Chapter 2

Electron (Hole) Confinement in Quantum Dots

In this chapter, the basic models and concepts of the carriers (electron and hole) confinement of quantum dots in finite and harmonic wells are presented, and related topics such as the single-band effective mass approximation (EMA) model of the Schrödinger equation, the discretization of Schrödinger equation, the pseudopotential method, the 8-band $\mathbf{k}\cdot\mathbf{p}$ method, and several realistic and refined confinement potentials applicable to quantum dots.

2.1 Introduction

Quantum dots as confined few- or many-particle quantum systems have various interesting analogies in physics [Griffiths, 2005, Vorrath and Blumel, 2003, Wigner, 1934, Merkt et al., 1991, Wood and Ashcroft, 1982, Thomson, 1904, Wang and Zunger, 1994b, Sun et al., 2002]. Historically viewed, before the advent of quantum mechanics and the atomic model of Bohr and Rutherford, the English physicist Thomson [1904] proposed his plum-pudding model, where (classical) electrons move in the homogeneous positive background charge which is distributed all over the atom. In real atoms, the strong Coulomb potential of the point-like nucleus gives rise to the shell structure of the periodic table of elements. Also, for atomic nuclei, a shell structure has been found with “magic numbers” of nucleons for very stable configurations. Clusters are systems of several to a few thousand atoms that have quite different properties with respect to the bulk or the single atom. Clusters of alkali atoms can be properly described within the Jellium model which is a quantum-mechanical version of the Thomson atom.

The band gap energy, some classical simplified analytical solutions to particle inside the infinite well and finite well, the pseudopotential method, the effective mass

approximation (EMA), the 8-band **k.p** method, and the confinement potentials are briefly described.

2.2 Band gap energy

The band gap of a semiconductor is, by definition, the energy necessary to create an electron (e^-) and hole (h^+) at rest, with respect to the lattice, and far enough apart so that their Coulomb attraction is negligible. If one carrier approaches the other, they may form a bound state (Wannier exciton) approximately described by a hydrogenic Hamiltonian $[\hat{H} = -\frac{\hbar^2}{2m_h^*}\nabla_h^2 - \frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{e^2}{\epsilon_r|r_e-r_h|}]$ at an energy slightly below the band gap. Here m_e^* and m_h^* are the effective masses of the electron and hole respectively, and ϵ_r the semiconductor dielectric constant. The effective masses of the two charges are often only a small fraction of an electron mass. Small masses naturally imply that localization energies for the hole and electron are large. The dielectric constant in semiconductors is typical, implying that Coulomb attraction is almost entirely screened. This combination of small masses and weak attraction causes the exciton wave function to extend over a large region. For example, the lowest 1S exciton of CdS has a diameter of about 60Å in the center of mass coordinate system.

In terms of a hydrogen atom analogy, the band gap is the ionization limit of the hydrogenic electron-hole bound states. Photon absorption at higher energies creates “free” electrons and holes with excess kinetic energies inside the semiconductor.

Brus [1983] suggested that the size of the 1S exciton provides a natural, intrinsic measure of linear dimension at which crystallite size effects will create a qualitatively different situation. As the crystallite approaches this size, the electron and hole interactions with the crystallite surfaces will dominate the dynamics. In this “molecular” limit, the energy level scheme will depend upon the size and shape of the crystallite, as well as the nature of the material. There will be a series of excited, discrete bound states approaching an ionization limit corresponding to the positively charged crystallite and a free electron in vacuum. The crystal is essentially not large enough for the intrinsic band gap to form, i.e., to sustain noninteractive, Bloch-type plane wave electron and hole eigenstates at band edges.

2.3 Finite potential well

The Schrödinger formalism shall be applied here to a simple particle in finite potential well with appropriate simplifying approximations.

Consider a particle of mass m held in a one-dimensional potential $V(x)$. Suppose that in some region $V(x)$ is constant, $V(x) = V$. For the region, we can find the stationary states of the particle when (a) $E > V$, b) $E < V$, and (c) $E = V$, where E is the energy of the particle.

(a) The stationary states are the solutions of

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V\phi(x) = E\phi(x) \quad (2.1)$$

For $E > V$, we introduce the positive constant k defined by $\hbar^2 k^2 / 2m = E - V$, so that

$$\frac{\partial^2 \phi(x)}{\partial x^2} + k^2 \phi(x) = 0 \quad (2.2)$$

The solution of this equation can be written in the form

$$\phi(x) = Ae^{ikx} + A'e^{-ikx} \quad (2.3)$$

where A and A' are arbitrary complex constants.

(b) For $E < V$, we introduce the positive constant ρ defined by $\hbar^2 \rho^2 / 2m = V - E$,

$$\frac{\partial^2 \phi(x)}{\partial x^2} - \rho^2 \phi(x) = 0 \quad (2.4)$$

The general solution is $\phi(x) = Be^{\rho x} + B'e^{-\rho x}$ where B and B' are arbitrary complex constants.

(c) When $E = V$ we have $\frac{\partial^2 \phi(x)}{\partial x^2} = 0$, so $\phi(x)$ is a linear function of x , $\phi(x) = Cx + C'$ where C and C' are complex constants.

2.3.1 1D finite well

Here, we study the bound states for a finite potential well defined by

$$V(x) = \begin{cases} 0 & (x < -a/2) & I \\ -V_0 & (-a/2 < x < a/2) & II \\ 0 & (a/2 < x) & III \end{cases} \quad (2.5)$$

The stationary states are the solutions of

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \phi(x)}{\partial x^2} + V\phi(x) = E\phi(x) \quad (2.6)$$

We write the stationary solutions for a particle of mass m and energy $-V_0 < E < 0$ for each of the regions. Defining

$$\rho = \sqrt{\frac{-2mE}{\hbar^2}} \quad k = \sqrt{\frac{2m(E+V_0)}{\hbar^2}} \quad (2.7)$$

Then the stationary solutions for each region are,

$$\begin{cases} \phi_I(x) = Ae^{\rho x} + A'e^{-\rho x} \\ \phi_{II}(x) = Be^{ikx} + B'e^{-ikx} \\ \phi_{III}(x) = C'e^{\rho x} + Ce^{-\rho x} \end{cases} \quad (2.8)$$

Since $\phi(x)$ and $\phi'(x) \equiv \frac{d\phi}{dx}$ must be bounded in regions I and III , $A' = C' = 0$; therefore,

$$\begin{aligned} \phi_I(x) &= Ae^{\rho x} \\ \phi_{II}(x) &= Be^{ikx} + B'e^{-ikx} \\ \phi_{III}(x) &= Ce^{-\rho x} \end{aligned} \quad (2.9)$$

The continuity of $\phi(x)$ at $x = -a/2$ yields

$$\begin{cases} Ae^{-\rho a/2} = Be^{-ika/2} + B'e^{ika/2} \\ \rho Ae^{-\rho a/2} = ikBe^{-ika/2} - ikB'e^{ika/2} \end{cases} \quad (2.10)$$

Similarly, the matching conditions at $x = a/2$ yield,

$$\begin{cases} Ce^{-\rho a/2} = Be^{ika/2} + B'e^{-ika/2} \\ -\rho Ce^{-\rho a/2} = ikBe^{ika/2} - ikB'e^{-ika/2} \end{cases} \quad (2.11)$$

Hence we can express B and B' in terms of A ,

$$B = \left(\frac{\rho + ik}{2ik} e^{(-\rho + ik)a/2} \right) A \quad B' = \left(-\frac{\rho - ik}{2ik} e^{(-\rho + ik)a/2} \right) A \quad (2.12)$$

Substitution of Equation (2.12) into Equation (2.11) gives

$$\begin{cases} C = \left(\frac{\rho + ik}{2ik} e^{ika} - \frac{\rho - ik}{2ik} e^{-ika} \right) A \\ -\frac{\rho}{ik} C = \left(\frac{\rho + ik}{2ik} e^{ika} - \frac{\rho - ik}{2ik} e^{-ika} \right) A \end{cases} \quad (2.13)$$

To obtain a non-vanishing solution,

$$-\frac{\rho}{ik} \left(\frac{\rho + ik}{2ik} e^{ika} - \frac{\rho - ik}{2ik} e^{-ika} \right) = \left(\frac{\rho + ik}{2ik} e^{ika} + \frac{\rho - ik}{2ik} e^{-ika} \right) \quad (2.14)$$

which is equivalent to

$$\left(\frac{\rho - ik}{\rho + ik}\right)^2 = e^{2ika} \quad (2.15)$$

Equation (2.15) is an equation for E , since ρ and k depend only on E and on the constants of the problem. The solutions in terms of E are the energies corresponding to bound states of the well.

We shall transform Equation (2.15) in terms of k only. There are two possible cases. The first case is

$$\text{Case 1} \quad \left(\frac{\rho - ik}{\rho + ik}\right)^2 = -e^{ika} \quad (2.16)$$

The left-hand side is a complex number of modulus 1 and phase $-2 \tan^{-1}(k/\rho)$. $(\rho + ik)$ is the complex conjugate of $(\rho - ik)$. The right-hand side is also a complex number of modulus 1 and its phase is $\pi + ka$ ($-e^{-ika} = e^{i\pi} \cdot e^{ika} = e^{i(\pi+ka)}$).

Therefore

$$\begin{aligned} \tan^{-1} \left(\frac{k}{\rho} \right) = - \left(\frac{\pi}{2} + \frac{ka}{2} \right) &\Rightarrow \frac{k}{\rho} = \tan \left[- \left(\frac{\pi}{2} + \frac{ka}{2} \right) \right] = - \tan \left(\frac{\pi}{2} + \frac{ka}{2} \right) = \\ &= \cot \left(\frac{ka}{2} \right) = \frac{1}{\tan(ka/2)} \end{aligned} \quad (2.17)$$

and

$$\tan \left(\frac{ka}{2} \right) = \frac{\rho}{k} \quad (2.18)$$

Defining $k_0 = \sqrt{\frac{2mV_0}{\hbar^2}} = \sqrt{k^2 + \rho^2}$, where the parameter k_0 is E -independent, and considering

$$\frac{1}{\cos^2(\frac{ka}{2})} = 1 + \tan^2 \left(\frac{ka}{2} \right) = \frac{k^2 + \rho^2}{k^2} = \left(\frac{k_0}{k} \right)^2 \quad (2.19)$$

Equation (2.16) is thus equivalent to the following system of equations:

$$\begin{cases} |\cos(\frac{ka}{2})| = \frac{k}{k_0} \\ \tan(\frac{ka}{2}) > 0 \end{cases} \quad (2.20)$$

where Equations (2.18) and (2.19) were used together with the fact that both ρ and k are positive.

For the second possible case,

$$\text{Case 2} \quad \left(\frac{\rho - ik}{\rho + ik}\right)^2 = e^{ika} \quad (2.21)$$

A similar argument leads to

$$-2 \tan^{-1} \left(\frac{k}{\rho} \right) = ka \Rightarrow \tan \left(\frac{ka}{2} \right) = -\frac{k}{\rho} \quad (2.22)$$

Consider

$$\sin^2 \left(\frac{ka}{2} \right) = \frac{\tan^2 \left(\frac{ka}{2} \right)}{1 + \tan^2 \left(\frac{ka}{2} \right)} = \frac{k^2}{k^2 + \rho^2} \quad (2.23)$$

Thus,

$$\begin{cases} |\sin \left(\frac{ka}{2} \right)| = \frac{k}{k_0} \\ \tan \left(\frac{ka}{2} \right) < 0 \end{cases} \quad (2.24)$$

We can solve analytically or represent Equation (2.24) graphically. The intersections represent the solutions in terms of k . From these solutions it is possible to determine the possible energies. We see that if $k_0 \leq \pi/a$, that is, if

$$V_0 \leq V_1 \equiv \frac{\pi^2 \hbar^2}{2ma^2} \quad (2.25)$$

then there exists only one bound state of the particle. If $V_1 \leq V_0 < 4V_1$ there are two bound states and so on. If $V_0 \gg V_1$, the slope $1/k_0$ of the straight line is very small. For the lowest energy levels we have approximately

$$k = \frac{n\pi}{a} \quad (n = 1, 2, 3, \dots) \quad (2.26)$$

and consequently,

$$E_n = \frac{\pi^2 \hbar^2 n^2}{2ma^2} - V_0 \quad (n = 1, 2, 3, \dots) \quad (2.27)$$

2.4 Harmonic confinement

2.4.1 1D harmonic confinement

We consider a particle moving under the harmonic potential,

$$H = \frac{p^2}{2m} + \frac{kx^2}{2} \quad (2.28)$$

where $k = m\omega^2$. The variable ω and m are respectively the angular frequency and the mass of the oscillator. Thus

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{m\omega^2}{2} x^2 \quad (2.29)$$

and the stationary Schrödinger equation is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + \frac{m\omega^2}{2} x^2 \psi(x) = E\psi(x) \quad (2.30)$$

The eigenfunctions that are the solutions of the Schrödinger equation are

$$\psi_n(x) = \left(\frac{1}{\pi\lambda^2} \right)^{1/4} \frac{1}{\sqrt{2^n n!}} H_n \left(\frac{x}{\lambda} \right) e^{-x^2/2\lambda^2} \quad (2.31)$$

where $\lambda = \sqrt{\hbar/m\omega}$ and $H_n(\varsigma)$ are the Hermite polynomials. The eigenvalues of the harmonic oscillator that are the eigenenergies are

$$E_n = \left(n + \frac{1}{2} \right) \hbar\omega \quad (n = 1, 2, 3, \dots) \quad (2.32)$$

The Hermite polynomial $H_n(\varsigma)$ is a polynomial of degree n that is symmetric for even n and antisymmetric for odd n . The Hermite polynomial is a solution of the differential equation

$$\frac{d^2 H_n(\varsigma)}{d\varsigma^2} + 2\varsigma \frac{dH_n(\varsigma)}{d\varsigma} - \left(\frac{2E_n}{\hbar\omega} - 1 \right) H_n(\varsigma) = 0 \quad (2.33)$$

which can be reduced to

$$\frac{d^2 H_n(\varsigma)}{d\varsigma^2} - 2\varsigma \frac{dH_n(\varsigma)}{d\varsigma} + 2nH_n(\varsigma) = 0 \quad (2.34)$$

The Hermite polynomials also satisfy the following relations,

$$\frac{dH_n(\varsigma)}{d\varsigma} = 2nH_{n-1}(\varsigma) \quad (2.35)$$

and

$$H_{n+1}(\varsigma) = 2\varsigma H_n(\varsigma) - 2nH_{n-1}(\varsigma) \quad (2.36)$$

The generating function of the Hermite polynomials is

$$S(\varsigma, t) = e^{-t^2 + 2t\varsigma} = \sum_{n=0}^{\infty} \frac{H_n(\varsigma)}{n!} t^n \quad (2.37)$$

and

$$H_n(\varsigma) = \frac{d^n}{dt^n}[S(\varsigma, t)] \quad (2.38)$$

2.4.2 2D/3D harmonic confinement

Similar to the one-dimensional case, the Hamiltonian in the two-dimensional case is

$$H_2 = \frac{p_x^2 + p_y^2}{2m} + \frac{m\omega^2 x^2}{2} + \frac{m\omega^2 y^2}{2} \quad (2.39)$$

In this case the Hamiltonian is separable in x and y , and the problem can be reduced to two one-dimensional harmonic oscillators, one in x and the other in y . The eigenfunctions in this case are

$$\psi_{n_x n_y}(x, y) = \psi_{n_x}(x) \psi_{n_y}(y) \quad (2.40)$$

where $\psi_{n_i}(x_i)$ is the eigenfunction of the one-dimensional harmonic oscillator. The eigenvalue corresponding to $\psi_{n_x n_y}(x, y)$ is

$$E_{n_x n_y} = \hbar\omega_x(n_x + \frac{1}{2}) + \hbar\omega_y(n_y + \frac{1}{2}) \quad (2.41)$$

The generalization to the three-dimensional case is therefore

$$E_{n_x n_y n_z} = \hbar\omega_x(n_x + \frac{1}{2}) + \hbar\omega_y(n_y + \frac{1}{2}) + \hbar\omega_z(n_z + \frac{1}{2}) \quad (n = 0, 1, 2, \dots) \quad (2.42)$$

2.5 Analytical and numerical methods for quantum dots

Quantum dots, or artificial atoms, have been the subject of intense experimental and theoretical research over the last few years, motivated by the physical effects and the potential device applications, both as electronic memories as well as optoelectronic devices.

Different methods have been used to study the energy spectrum and correlation effects of interacting electrons confined in quantum dots under the effect of an applied

magnetic field. In most published works, authors model the quantum dot as a two-dimensional disk, since the confinement in the z -direction is assumed to be stronger than in the xy -plane. Zhu et al. [1990] studied the effect of dimensionality on the spectra of two electrons confined with parabolic potentials by considering two-dimensional and three-dimensional quantum dots. They showed that the electron-electron coulomb interaction energy strongly depends on the dimensionality of the quantum dots, and the spectra differ dramatically.

There have been many theoretical works about the electronic structures of quantum dots. Several theoretical approaches have been used in these studies.

One is the continuum **k.p** effective-mass method. This is the most widely used method, borrowed from bulk quantum well and exciton studies. However, this method has several shortcomings, especially for small colloidal nanocrystals. For example, the small sizes of the quantum dots might be beyond the valid range of the continuum **k.p** model in reciprocal space, and there is also an ambiguity for the **k.p** boundary condition.

The second widely used method in nanostructure calculation is the tight-binding model. The tight-binding model can be used to study thousand-atom systems easily, and it has been proven to be highly successful. However, it is sometimes difficult to fit the conduction band band structure. In addition, there is no information about the atomic features of the wave functions.

The third method for nanocrystal study is the empirical pseudopotential method (EPM). The original EPM was developed in the 1960's to describe the bulk band structures of semiconductors; it uses a sum of non-self-consistent screened pseudopotentials to represent the total potential of a system, and it also uses a variationally flexible plane wave basis to describe the electron wave function. Recently, the EPM has been adapted to calculate nanocrystals. It has also been improved by:

1. fitting it to the ab initio bulk potentials;
2. adding local environment-dependent prefactors to describe the deformation potentials; and
3. rescaling the kinetic energy operator to mimic the effects of nonlocal potentials.

These improvements have allowed the accurate description of the electronic structure of nanosystems. Despite the success of the EPM method, there are still problems that need to be resolved. One problem of the EPM calculation for free-standing colloidal systems is the surface passivation. While it is easy to fit a bulk EPM, it is often difficult to find the corresponding surface passivation potentials. As

a result, the EPM method and its improved version, semiempirical pseudopotential method (SEPM), have been limited to a few semiconductor materials (e.g., Si, Ge, InAs, InP, CdSe) for colloidal nanocrystal studies.

The fourth method to calculate the electronic structure of a nanocrystal is to use *ab initio* methods, such as the density functional theory (DFT). This method is more reliable than the EPM approach and can be used for almost any material. One disadvantage of this method is the large computational time required for thousand atom nanostructure calculations. Besides, if the DFT method with the local density approximation (LDA) is used, there is often a band gap problem that needs to be addressed.

Solving the state of an interacting N -electron system requires solving the N -particle Schrödinger equation $H\Psi = E\Psi$; where Ψ is the wave function of all particles, H the Hamiltonian operator, and E the total energy. Solving this equation analytically is possible only in special cases, and solving it numerically is almost as difficult: already the general case of two-particles in two dimensions, giving four degrees of freedom, is challenging. For increasing degrees of freedom, it soon becomes impossible to store just the numerical values of the wave function (on a grid of reasonable spacing) in a computer's memory space.

However, it may be possible to get past the difficulties in solving the interacting Schrödinger equation. As the difficulties emerge from interactions, various mean-field theories take the interactions into account only in an averaged way. The widely used density-functional theory and the Hartree-Fock methods belong to this class.

With increasing computational power, methods which solve the wave function exactly have become increasingly popular. These methods treat interaction effects accurately. The exact-diagonalization method aims at solving the Schrödinger equation to a specified numerical accuracy, by using a suitably chosen basis set. The number of particles is, however, severely limited by the rapidly increasing basis size. Various Monte Carlo methods, on the other hand, use a statistical approach, which are in principle accurate, and can be applied in some cases to systems containing up to several thousand particles.

2.6 Single-band effective mass approximation method, EMA

Here we justify the use of electron and hole effective masses to replace the free-space electron/hole masses.

The theory of quantum nanostructures has been dominated mainly by a single approach so widely used: the effective-mass approximation (EMA) and its extension to the $\mathbf{k}\cdot\mathbf{p}$ (where $\mathbf{k}$ is the wave vector and $\mathbf{p}$ is the momentum) method. The essential idea is sweeping in its simplicity. The single-particle wave functions $\psi_i(r)$ of three-dimensional (3D)-periodic bulk, two-dimensional (2D)-periodic film/well, one-dimensional (1D)-periodic wires, or zero-dimensional (OD)-periodic dot, are expanded by a handful of 3D-periodic Bloch orbitals taken from the Brillouin zone center (Γ point) of the underlying bulk solid. The physical accuracy of this representation is naturally highest for systems closest to the reference from which the basis functions are drawn (Γ point of the 3D bulk). It decreases as one moves away from the Brillouin zone center and as dimensionality is reduced in the sequence $3D \rightarrow 2D \rightarrow 1D \rightarrow OD$.

We then solve the following Schrödinger equation

$$\left\{ -\frac{1}{2}\nabla^2 + V(r) \right\} \psi_i(r) = \varepsilon_i \psi_i(r) \quad (2.43)$$

for a given geometry and given pseudopotential. This is nontrivial for $N = 10^3 - 10^5$ atom systems because the number of planewave basis functions in scales in the order of N [denoted $O(N)$]. For most semiconducting systems made up of main-group elements, one needs about 50 plane waves per atom. So for $N = 1,000$, one typically has a $50,000 \times 50,000$ Hamiltonian size. The conventional variational approach is to minimize the energy $\langle \psi | \hat{H} | \psi \rangle$ by varying the expansion coefficients; the first ψ obtained is then the lowest energy eigenstate of $\hat{H}$. To find a higher state, one needs to orthogonalize ψ to all previously converged energy eigenstates below it. The effort needed to accomplish this orthogonalization scales to N^3 . Consequently only small systems ($N < 100$ atoms) can be conveniently addressed by such conventional methods. However in order to study, for example, the near-edge optical properties of semiconductor quantum structures, one does not really need to know the 10^3 to 10^6 higher states.

2.7 Discretization of the Schrödinger equation

Suppose we have a complete set of orthonormal functions $\phi_n(x)$ and we are interested in solving a (single-particle) Schrödinger equation $\hat{H}\psi(x) = E\psi(x)$. We can expand any function of x in terms of a complete orthonormal set $\phi_n(x)$

$$\psi(x) = \sum_{n=0}^{\infty} a_n \phi_n(x) \quad (2.44)$$

$\psi(x)$ can equivalently be determined with the coefficients a_n of the expansion

$$\psi(x) \Leftrightarrow \{a_n\} \Leftrightarrow \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \quad (2.45)$$

For a proper normalization we require $\sum_{n=0}^{\infty} |a_n|^2 = 1$. Now, the Schrödinger equation $\hat{H}\psi(x) = E\psi(x)$ can be written with the set $\phi_n(x)$

$$\hat{H} \left(\sum_n a_n \phi_n(x) \right) = E \left(\sum_n a_n \phi_n(x) \right) \quad (2.46)$$

Multiplying the left hand side by $\phi_m^*(x)$ and integrating over the domain, we obtain

$$\begin{aligned} \int \phi_m^*(x) \hat{H} \left(\sum_n a_n \phi_n(x) \right) dx &= \int \phi_m^*(x) E \left(\sum_n a_n \phi_n(x) \right) dx \\ \sum_n a_n \langle \phi_m | \hat{H} | \phi_n \rangle &= E \sum_n a_n \underbrace{\langle \phi_m | \phi_n \rangle}_{\delta_{n,m}} \end{aligned} \quad (2.47)$$

We assume a shorthand notation for the matrix element,

$$\langle \phi_m | \hat{H} | \phi_n \rangle = H_{nm} \quad (2.48)$$

and now we can write the Schrödinger equation in a matrix form,

$$\begin{pmatrix} H_{11} & H_{12} & H_{13} & \cdots \\ H_{21} & H_{22} & H_{23} & \cdots \\ H_{31} & H_{32} & H_{33} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \quad (2.49)$$

We have thus formulated the problem of finding the eigenvalues and eigenvectors of the Hamiltonian $\hat{H}\psi = E\psi$ in the matrix presentation. The solution of the Schrödinger equation is equivalent to finding the eigenvalues and eigenvectors of the matrix. If we had chosen the basis ϕ_n to be the solutions of the single-particle Hamiltonian $\hat{H}\phi_n = E_n\phi_n$ and used those states in the expansion, we would have

$$H_{nm} = \langle \phi_m | \hat{H} | \phi_n \rangle = \langle \phi_m | E_n | \phi_n \rangle = E_n \delta_{nm} \quad (2.50)$$

Then our matrix is already diagonal and energy eigenvalues can be read imme-

diately from the diagonal of the matrix,

$$\begin{pmatrix} E_1 & 0 & 0 & \cdots \\ 0 & E_2 & 0 & \cdots \\ 0 & 0 & E_3 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} = E \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{pmatrix} \quad (2.51)$$

The matrix equation can be satisfied only if

$$\det(H - EI) = \det \begin{vmatrix} E_1 - E & 0 & 0 & \cdots \\ 0 & E_2 - E & 0 & \cdots \\ 0 & 0 & E_3 - E & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \quad (2.52)$$

If we do not know the solution of the Schrödinger equation, we can express the Hamiltonian in the matrix formulation with any complete basis we wish to choose and the eigenvalues and vectors can be found by diagonalizing the Hamiltonian. However, the matrix is theoretically infinite, whereas in the actual calculations we include only a certain finite number of states in the expansion and then diagonalize the matrix in a truncated basis. The convergence can be checked by adding more states ϕ_n in the expansion and studying the change in the eigenvalues as the basis size and the matrix dimensions are increased.

In the case of interacting electrons, we can expand the many-electron wave function using a set of basis functions. According to quantum theory, these basis functions must be antisymmetric (for fermion). The problem also can be formulated in matrix form for an interacting few-particle system. Suppose we have a complete set of N -particle wave functions Φ_c (the set of determinants with all possible combinations of different single-particle states c), we can search the solution for the interacting few-particle Hamiltonian

$$\hat{H}\Psi = (\hat{H}_0 + \hat{H}_C)\Psi = E\Psi \quad (2.53)$$

by expanding the wave function Ψ in this basis,

$$\Psi = \sum_c A_c \Phi_c \quad (2.54)$$

where the summation runs over all possible determinant wave functions.

2.8 FEM and the discretization of the Schrödinger equation

The application of the finite element method (FEM) to the electronic structure of isolated atomic and molecular systems began to appear in the 1970s. Almost two decades later, Linderberg [1987] and White et al. [1989] applied the method to full three-dimensional atomic and molecular calculations.

The FEM [Zienkiewicz, 1977, Pask et al., 1999, Beck, 2000, Pask and Sterne, 2005, Torsti et al., 2006] is a general approach for the solution of differential and integral equations which uses a strictly local, piecewise-polynomial basis. As the basis is strictly local in real space, the method allows for variable resolution in real space, produces sparse and structured matrices, and enable the effective use of iterative solution methods. The FEM combines significant advantages of both real-space-grid and basis-oriented approaches.

The FEM is a variational expansion approach, in which solutions are represented as a linear combination of basis functions. It employs a basis of strictly local piecewise polynomials, each overlapping only its immediate neighbors. As the basis is composed of polynomials, the method is completely general and its accuracy can be improved systematically. As the FE basis is strictly local, the method offers some significant advantages with respect to large-scale calculations: (1) the FE basis functions are localized, they can be concentrated where needed in real space to increase the efficiency of the representation; (2) the FE method can accommodate a wide variety of boundary conditions: Dirichlet boundary conditions for molecules or clusters, Bloch boundary conditions for crystals, a mixture of these for surfaces; (3) most significantly for large-scale calculations, the strict locality of the FE basis facilitates implementation on massively parallel computational architectures by minimizing the need for nonlocal communications.

The main computational task is to numerically solve the single-particle Schrödinger partial differential equation of the form

$$\hat{H}\psi_i = \epsilon_i\psi_i \quad (2.55)$$

where $\hat{H}$ is a Hamiltonian operator, ψ_i and ϵ_i are the single-particle orbitals and eigenvalues, respectively.

The main idea in variational methods for solving partial differential equations is to multiply the equation by a test function and then integrate the identity over

the computational domain. This leads us to our eigenvalue problem. In the FEM implementations, an integration by parts of the Laplacian is performed to obtain a symmetric bilinear form, and to treat the boundary terms in a natural way. Thus, with the example Hamiltonian, the bilinear form for the FEM implementation can be written as

$$a_{fe}(\psi, \eta) = \int \left(\frac{1}{2} \nabla \psi(\mathbf{r}) \cdot \nabla \eta(\mathbf{r}) + V(r) \psi(\mathbf{r}) \eta(\mathbf{r}) + \sum_i^N c_i \xi_i(\mathbf{r}) \int \xi_i(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} \eta(\mathbf{r}) \right) d\mathbf{r} + \text{boundary terms} \quad (2.56)$$

and the variational eigenproblem becomes

$$a_{fe}(\psi, \eta) = \epsilon(\psi, \eta) \quad (2.57)$$

for all test functions η .

The discretization in variational methods is obtained simply by choosing finite-dimensional spaces V^h and T^h to approximate the functions ψ and η in the above eigenproblems. Then one obtains with trial functions

$$\{\psi_j\}_{j=1}^n, \quad \psi_j \in V_h \quad (2.58)$$

and with test functions

$$\{\eta_j\}_{j=1}^n, \quad \eta_j \in T_h \quad (2.59)$$

The Petrov-Galerkin condition is thus obtained whereby $a_{fe}(\psi_h, \eta_k) = \epsilon_h(\psi_h, \eta_k)$, $k = 1, \dots, n$, where $\psi_h = \sum_{j=1}^n c_j \psi_j$. This leads to a finite-dimensional generalized eigenvalue problem

$$H\mathbf{c} = \epsilon S\mathbf{c} \quad (2.60)$$

where H is the discretized Hamiltonian, $H_{ij} = a_{fe}(\psi_j, \eta_i)$, S is the overlap matrix, $S_{ij} = (\psi_j, \eta_i)$, and $\mathbf{c}$ is the vector of the unknown coefficients c_j .

In variational methods it is important to consider the choice of the finite-dimensional subspaces V_h and T_h . In the FEM here, we follow the usual convention and select $V_h = T_h$.

The FEM allows different geometries and boundary conditions to be implemented in a straightforward way, and the possibility to employ higher-order polynomials in the basis to reduce the total number of basis functions used. In the FEM, the calculation domain is divided into elements which can be progressively refined to achieve mesh independence. In three dimensional calculations tetrahedral, hexahedral and pyramid-shaped elements are used. The pyramids are needed to combine the meshes consisting of hexahedra and tetrahedra together. The hexahedral (box-shaped) elements are good if the calculation volume is needed to be filled uniformly. And the tetrahedra have the advantage that the size can easily vary inside the domain region to increase the accuracy in the core regions of the atoms.

2.9 Other useful methods

2.9.1 Pseudopotential method

In this section we outline an approximation which is based upon the observation that the core electrons are relatively unaffected by the chemical environment of an atom. Thus we assume that their contribution to the total binding energy does not change when isolated atoms are brought together to form a molecule or crystal. The actual energy differences of interest are the changes in valence electron energies, and so if the binding energy of the core electrons can be subtracted out, the valence electron energy change will be a much larger fraction of the total binding energy, and hence much easier to calculate accurately. We also note that the strong nuclear Coulomb potential and highly localized core electron wave functions are difficult to represent computationally. Since the atomic wave functions are eigenstates of the atomic Hamiltonian, they must all be mutually orthogonal. Also, since the core states are localized in the vicinity of the nucleus, the valence states must oscillate rapidly in this core region in order to maintain this orthogonality with the core electrons. This rapid oscillation results in a large kinetic energy for the valence electrons in the core region, which roughly cancels the large potential energy due to the strong Coulomb potential. Thus the valence electrons are much more weakly bound than the core electrons. It is therefore convenient to attempt to replace the strong Coulomb potential and core electrons by an effective pseudopotential which is much weaker, and replace the valence electron wave functions, which oscillate rapidly in the core region, by pseudo wave functions which vary smoothly in the core region.

In the pseudopotential approach [Pryor et al., 1998, Canning et al., 2000, Chelikowsky and Cohen, 1976, Zunger, 2001] the wave function, $\psi_i(r)$, is a solution of the following Schrödinger equation,

$$\left(-\frac{1}{2}\nabla^2 + \sum_{n\alpha} \hat{v}_\alpha(r - R_{n\alpha})\right) \psi_i(x) = \varepsilon_i \psi_i(x), \quad (2.61)$$

where $\hat{v}_\alpha(r - R_{n\alpha})$ is the pseudopotential of atomic type α and $R_{n\alpha}$ is the relaxed position of the n^{th} atom of type α . The relaxed atomic positions are determined by minimizing the atomistic elastic energy as described by the valence force field (VFF) method. The atomic pseudopotentials $\{v_\alpha\}$ are strain dependent and are carefully fitted to the measured bulk band gaps, effective masses and to first-principle calculations of the band offsets and deformation potentials. The wave functions $\psi(r)$ are expanded in a plane wave basis set. Eigenstates are then calculated using the diagonalization method.

2.9.2 8-Band k.p Method

Strained-induced confinement potential

The form of the Hamiltonian describing the behavior of the single charge carrier is given by Luttinger and Kohn [1955] and is derived from **k.p** theory [Pryor, 1998, Stier et al., 1999, Wang et al., 2000b]. Within this framework, the single charge carrier behaves according to the Schrödinger equation and can be written as

$$-\frac{\hbar^2}{2m} \nabla_i L_{ij}^{\alpha\beta} \nabla_j \psi^\beta + V^{\alpha\beta} \psi^\beta = E \psi^\alpha \quad (2.62)$$

where ψ is the wave function of the carrier, V the spatially varying potential field through which the charge carrier does work, and L the Luttinger-Kohn Hamiltonian containing the effective mass tensor parameters. The indices α and β represent the energy sub-bands that form a basis for the wave function of the charge carrier; this basis may include 1, 2, 4, 8, or more sub-bands within the conduction and valence bands of the material. A larger sub-band basis increases the energy accuracy of the calculation but at a computational cost of the order of the square of the number of sub-bands.

The potential field V is input to the calculation based on the local composition of the material and the local state of strain in the material. (Other possible contributions to V include an applied electric potential or a piezoelectric potential).

Thus, V can be written as

$$V^{\alpha\beta} = V_{comp}^{\alpha\beta} + V_{strain}^{\alpha\beta} \quad (2.63)$$

where the compositional contribution of the potential is due to the energy band misalignment between adjacent layers (e.g., dot layer/capping layer) in the heterostructure. This contribution ranges from 0.1 to 1.5 eV depending on the layer compositions and the sub-bands under consideration. The strain portion of the potential couples the elasticity problem to the quantum mechanical behavior of the charge carrier. This coupling is quantified through deformation potential theory, which converts an elastic strain ε_{ij} into an electrostatic potential $V_{strain}^{\alpha\beta}$ through the scalar product given by

$$V_{strain}^{\alpha\beta} = D_{ij}^{\alpha\beta} \varepsilon_{ij} \quad (2.64)$$

where $D_{ij}^{\alpha\beta}$ is the deformation potential tensor field in the material, which is a local material property. The components of the deformation potential tensor have values in the order of 1-10 eV. Thus, depending on the local composition and strain, the elastic contribution may approach the magnitude of the compositional contribution to the electrostatic potential.

Electronic structure modified by strain-induced confinement potential

The electronic structure can be solved in the envelope approximation using the eight-band strain-dependent $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian, $H_k + H_S$ [Pryor, 1998]. The kinetic Hamiltonian is

$$H_k = \begin{pmatrix} A & 0 & V^* & 0 & \sqrt{3}V & -\sqrt{2}U & -U & \sqrt{2}V^* \\ 0 & A & -\sqrt{2}U & -\sqrt{3}V^* & 0 & -V & \sqrt{2}V & U \\ V & -\sqrt{2}U & -P+Q & -S^* & R & 0 & \sqrt{\frac{3}{2}}S & -\sqrt{2}Q \\ 0 & -\sqrt{3}V & -S & -P-Q & 0 & R & -\sqrt{2}R & \frac{1}{\sqrt{2}}S \\ \sqrt{3}V^* & 0 & R^* & 0 & -P-Q & S^* & \frac{1}{\sqrt{2}}S^* & \sqrt{2}R^* \\ -\sqrt{2}U & -V^* & 0 & R^* & S & -P+Q & \sqrt{2}Q & \sqrt{\frac{3}{2}}S^* \\ -U & \sqrt{2}V^* & \sqrt{\frac{3}{2}}S^* & -\sqrt{2}R^* & \frac{1}{\sqrt{2}}S & \sqrt{2}Q & -P-\Delta & 0 \\ \sqrt{2}V & U & -\sqrt{2}Q & \frac{1}{\sqrt{2}}S^* & \sqrt{2}R & \sqrt{\frac{3}{2}}S & 0 & -P-\Delta \end{pmatrix} \quad (2.65)$$

where

$$\begin{aligned}
 A &= E_c - \frac{\hbar^2}{2m_0} (\partial_x^2 + \partial_y^2 + \partial_z^2), \\
 P &= E_v - \gamma_1 \frac{\hbar^2}{2m_0} (\partial_x^2 + \partial_y^2 + \partial_z^2), \\
 Q &= -\gamma_2 \frac{\hbar^2}{2m_0} (\partial_x^2 + \partial_y^2 - 2\partial_z^2), \\
 R &= \sqrt{3} \frac{\hbar^2}{2m_0} [\gamma_2 (\partial_x^2 - \partial_y^2) - 2i\gamma_3 \partial_x \partial_y], \\
 S &= -\sqrt{3} \gamma_3 \frac{\hbar^2}{2m_0} \partial_z (\partial_x - i\partial_y), \\
 U &= \frac{-i}{\sqrt{3}} P_0 \partial_z, \\
 V &= \frac{-i}{\sqrt{6}} P_0 (\partial_x - i\partial_y).
 \end{aligned} \tag{2.66}$$

where δ is the usual partial differentiation notation, e.g. δ_x represents $\frac{\delta}{\delta x}$.

P_0 is the coupling between the conduction and valence bands, while E_c and E_v are the (unstrained) conduction and valence-band energies respectively, and Δ is the spin-orbit splitting. The γ_i 's are the modified Luttinger parameters, defined in terms of the usual Luttinger parameters, γ_i^L , by

$$\begin{aligned}
 \gamma_1 &= \gamma_1^L - \frac{E_p}{3E_g + \Delta} \\
 \gamma_2 &= \gamma_2^L - \frac{1}{2} \frac{E_p}{3E_g + \Delta} \\
 \gamma_3 &= \gamma_3^L - \frac{1}{2} \frac{E_p}{3E_g + \Delta}
 \end{aligned} \tag{2.67}$$

where $E_g = E_c - E_v$ is the energy gap, and $E_p = 2m_0 P_0^2 / \hbar^2$.

The strain enters through a matrix-valued potential that couples the various components

$$H_s = \begin{pmatrix} a_c e & 0 & -v^* & 0 & -\sqrt{3}v & \sqrt{2}u & u & -\sqrt{2}v^* \\ 0 & a_c e & \sqrt{2}u & -\sqrt{3}v^* & 0 & v & -\sqrt{2}v & -u \\ -v & \sqrt{2}u & -p+q & -s^* & r & 0 & \sqrt{\frac{3}{2}}s & -\sqrt{2}q \\ 0 & \sqrt{3}v & -s & -p-q & 0 & r & -\sqrt{2}r & \frac{1}{\sqrt{2}}s \\ -\sqrt{3}v^* & 0 & r^* & 0 & -p-q & s^* & \frac{1}{\sqrt{2}}s^* & \sqrt{2}r^* \\ \sqrt{2}u & v^* & 0 & r^* & s & -p+q & \sqrt{2}q & \sqrt{\frac{3}{2}}s^* \\ u & -\sqrt{2}v^* & \sqrt{\frac{3}{2}}s^* & -\sqrt{2}r^* & \frac{1}{\sqrt{2}}s & \sqrt{2}q & -a_v e & 0 \\ -\sqrt{2}v & -u & -\sqrt{2}q & \frac{1}{\sqrt{2}}s^* & \sqrt{2}r & \sqrt{\frac{3}{2}}s & 0 & -a_v e \end{pmatrix} \tag{2.68}$$

where

$$\begin{aligned}
 p &= a_v(e_{xx} + e_{yy} + e_{zz}), \\
 q &= b \left[e_{zz} - \frac{1}{2}(e_{xx} + e_{yy}) \right], \\
 r &= \frac{\sqrt{3}}{2}b(e_{xx} - e_{yy}) - ide_{xy}, \\
 s &= -d(e_{xz} - ie_{yz}), \\
 u &= \frac{-i}{\sqrt{3}}P_0 \sum_j e_{zj}\partial_j, \\
 v &= \frac{-i}{\sqrt{6}}P_0 \sum_j (e_{xj} - ie_{yj})\partial_j.
 \end{aligned} \tag{2.69}$$

and e_{ij} is the strain tensor, b and d the shear deformation potentials, a_v the hydrostatic valence-band deformation potential, and a_c the conduction-band deformation potential.

The energies and wave functions are computed by replacing derivatives with differences on the same cubic grid used for the strain calculation. The material parameters and strain vary from site to site. The Hamiltonian is then a sparse matrix which is easily diagonalized using the Lanczos algorithm. The calculation can be further simplified by eliminating unnecessary barrier material, since bound states fall off exponentially within the barrier.

2.10 Other confinement potentials

The effect of the confinement potential is dominant and in the range of 10's of eV. This section provides other models of the confinement potentials [Jost and Kohn, 1952] that are more refined when better precision is required, such as the gradient mixture of materials at the physical boundaries.

The most important parameter distinguishing one quantum mechanical problem from another is the potential energy term, $V(x)$. The energy gap between the valence and conduction band is of fundamental importance for the properties of a solid. Most of a material's behavior, such as intrinsic conductivity, optical transitions, or electronic transitions, depend on it. Any change of the gap may significantly alter the material's physics and chemistry. This occurs when the size of a solid is reduced to the nanometer length scale. Therefore, the scientific description and understanding of nanomaterials need to take into account a band gap which is different from that of the bulk.

In addition, effects such as structural changes, lattice contraction, atomic relaxation, surface reconstruction, surface passivation, or strain induced by a host material, can change the gap. The quantum size effect (QSE) predicts the formation of a band gap with decreasing particle size for metals and widening of the intrinsic

gap for semiconductors.

2.10.1 New Jellium model potential

There is a new refined Jellium model potential [Kotsos et al., 1999] with a variable parameter, β ,

$$V(r) = -\frac{U_0}{1 + (r/R)^\beta} \quad (2.70)$$

The depth U_0 of the potential well is chosen to be the sum of the Fermi energy and work-function, while the potential half-depth radius R is expressed in terms of the number of valence electrons N in the cluster, through the standard relationship $R = r_s N^{1/3}$, where r_s is the electron density parameter. Finally, β is a parameter determining the potential softness. The potential is of long range for small values of β . For $\beta = 1$ it approaches the Coulomb potential at large distances, while for $\beta = 2$ it is harmonic at small distances. As β becomes very large the potential approaches that of the rectangular well.

2.10.2 2D Bolton potential

Bolton [1995], assumed that the confinement potential is parabolic in the first approximation, where the potentials considered consisted of a parabolic background with a perturbation superimposed on it. The form of the non-parabolicity took into consideration the effect of the remote donor ions. Ordinarily the confinement of these donors give rise to a uniform Jellium of positive charge. However, owing to the discrete nature of these positive charges there might be some residual ripple superimposed on the parabolic Jellium potential. With this motivation, the ripples were modeled as a cosine perturbation giving rise to the following potential

$$V(x, y) = \frac{1}{2}m^*\omega_0^2 (x^2 + y^2) + \frac{C}{2} \sum_{i=1}^N \left[\cos\left(\frac{2\pi x}{\lambda}\right) + \cos\left(\frac{2\pi y}{\lambda}\right) \right], \quad (2.71)$$

where C determines the amplitude of the perturbation, and λ is its wavelength.

2.10.3 2D elliptic potential

Compared with circular quantum dots which have been studied by a variety of methods, rectangular quantum dots have attracted considerably less attention both experimentally and theoretically. Invariably, most calculations assume a pure two-dimensional confinement potential. Frequently, a model of two dimensional anisotropic harmonic oscillator potential,

$$\frac{1}{2}m^*(\omega_x^2 x^2 + \omega_y^2 y^2) \quad (2.72)$$

which is characteristic of an elliptic quantum dot with confinement strengths ω_x and ω_y in the x and y directions, respectively, is used in theoretical calculations for this purpose. Simulations conducted with such a potential showed that it is not straightforward process to match the experimental geometric aspect ratio $\beta=L/S$, where $L(S)$ is the length of the longest(shortest) side to the potential deformation ratio $\delta = \omega_y/\omega_x$.

2.10.4 2D harmonic + triangular deformation potential

The geometrical effect of an asymmetric confining potential was proposed by Ezaki et al. [1997]. The lateral confining potential, $V(x, y)$ of the 2DEG is modeled by the following equation

$$V(x, y) = \frac{1}{2}m^* (\omega_x^2 x^2 + \omega_y^2 y^2) \left\{ 1 + \alpha \frac{2}{7} \cos 3\phi \right\}, \quad (2.73)$$

where ω_x and ω_y are the confining energies along the x and y directions respectively, α ($= 0$ or 1) a parameter to specify the shape of the lateral confining potential, and ϕ the angle with respect to a specific axis in the $x - y$ plane. When $\alpha = 0$, the contour line of the lateral confining potential becomes an ellipse (for $\omega_x \neq \omega_y$) or a circle (for $\omega_x = \omega_y$). When $\alpha = 1$ and $\omega_x = \omega_y$ we obtained a triangular shaped confinement potential.

2.10.5 Gaussian confining potential

The electrons in a quantum dot have also been modeled with the Gaussian confining potential

$$V(r) = -V_0 e^{(-r^2/R^2)} \quad (2.74)$$

where the depth of the potential well $V_0 > 0$, and R is the range of the confinement potential, which corresponds to a radius of the quantum dot, $r = |r|$ where $r = (x, y)$ for the 2D system, and $r = (x, y, z)$ for the 3D system. For $r/R \ll 1$, the Gaussian potential can be approximated by the harmonic-oscillator parabolic potential $\tilde{V}(r) = -V_0 + \gamma^2 r^2$ where $\gamma^2 = V_0/R^2$.

2.11 Concluding remarks

We have done the literature research on the factors affecting carriers (electron, hole) confinement in the quantum dots. The changes of transition energies with size, shape and material compositions will be the focus of our research in subsequent chapters.

In the next chapter, the computational models of the simplified 2D-square quantum dot in infinite well, and the 3D pyramidal InAs/GaAs self-assembled quantum dots and 3D colloidal CdS quantum dots in finite well will be simulated and validated with known analytical, numerical and experimental data.

Chapter 3

Computational Modeling of Quantum Dots

In this chapter, we present the computational models of the effective mass approximation (EMA) and the finite width EMA (FWEMA) and solve the models numerically using the finite element method (FEM). We first model the 2D-square quantum dot in infinite well to validate the FEM method by comparing with the analytical results. Next, the 3D pyramidal self-assembled quantum dots in finite well are simulated and compared with the reported results of the finite-volume method. The results are in excellent agreement.

3.1 Introduction

Today there is little doubt that quantum theory [Kohn and Sham, 1965, Kohn and Mattsson, 1998, Kohn, 1999a,b] applied to electrons and atomic nuclei provides the foundation for all of low-energy physics, chemistry and biology, and that if we wish to describe complex processes occurring in real materials precisely, we should attempt to solve the equations of quantum mechanics. Unfortunately, the equations are too complicated to be solved analytically for all but the simplest and hence most trivial of systems. The only hope of bringing the power of quantum mechanics to bear on real phenomena of genuine interest to contemporary scientists and of relevance to our society in general is to solve the equations numerically by modeling the processes of interest computationally. During the past 20 years, various semiconductor nano-structures have been synthesized and it has been found that their electrical and optical properties are dramatically different from their bulk counterparts.

The quantum dot is generally called an artificial atom. It has electron shell structures which obey the Hund's filling rules. The difference between the real atom

and artificial atom is that there is a singularity (nucleus) in the real atom while the artificial atom is generally treated as homogeneous. There is a quantum size effect (QSE) energy dependence on the size of the quantum dot [Li et al., 2001a,b, Rodt et al., 2007, Zhang et al., 2007, Sattler, 2002].

3.2 1D quantum dots in infinite well

The Schrödinger equation for the 1D gallium arsenide (GaAs) in infinite well is given as

$$\begin{aligned}
 & -\frac{\hbar^2}{2m_e^*} \nabla_e^2 \psi(x) + V_e(x) \psi(x) = \varepsilon \psi(x) \\
 & \left\{ \begin{array}{l} m_e^* = 0.067 m_e \\ V_e(x) = \begin{cases} 0 & 0 \leq x \leq L \\ \infty & \text{elsewhere} \end{cases} \end{array} \right. \quad (3.1)
 \end{aligned}$$

where $|\psi(x)|$ is the electron envelop function in the x - direction, $\hbar$ the usual Planck constant, m_e^* the effective electron mass, $V_e(x)$ the electron confining potential, and ε the energy eigenvalues.

We simulate the 1D gallium arsenide (GaAs) quantum dot ($L=30.76\text{nm}$) in infinite well and solve the Schrödinger equation with the finite element method using a commercial FEM package. The meshing is done with the software and the resulting eigenvalue problem solved by the embedded Eigenvalue Solver.

The results of the energy levels for the ground to 19th excited states are given in Table 3.1 and compared with analytical results of the following Equation (3.2),

$$E_{n_x} = \frac{1}{2} (n_x^2) H_a^* \left\{ \begin{array}{l} n_x = 1, 2, 3, \dots \\ H_a^* = 11.8572 \text{ meV} \end{array} \right. \quad (3.2)$$

where n_x is the shell quantum number, and H_a^* the Hartree constant for GaAs [Rasanen et al., 2003]. The differences of energies between the simulation and analytical are less than 1.2 meV.

Table 3.1: Comparison of FEM simulation results (with 1024 elements) for 1D GaAs quantum dot against analytical method for electrons confined in an infinite barrier. The energy states for 20 states from the present FEM simulation and analytical method are listed.

FEM			Analytical		
State	Energy (eV)	n_x	E_{n_x} (eV)	Differences (meV)	%
ground	0.005932	1	0.0059286	0.0034	0.0573
1	0.023726	2	0.0237144	0.0116	0.0489
2	0.053384	3	0.0533574	0.0266	0.0498
3	0.094905	4	0.0948576	0.0474	0.0499
4	0.14829	5	0.148215	0.075	0.0506
5	0.213537	6	0.2134296	0.1074	0.0503
6	0.290648	7	0.2905014	0.1466	0.0504
7	0.379622	8	0.3794304	0.1916	0.0505
8	0.480459	9	0.4802166	0.2424	0.0505
9	0.593159	10	0.59286	0.299	0.0504
10	0.717722	11	0.7173606	0.3614	0.0504
11	0.854149	12	0.8537184	0.4306	0.0504
12	1.002438	13	1.0019334	0.5046	0.0504
13	1.162591	14	1.1620056	0.5854	0.0504
14	1.334607	15	1.333935	0.672	0.0504
15	1.518487	16	1.5177216	0.7654	0.0504
16	1.714229	17	1.7133654	0.8636	0.0504
17	1.921835	18	1.9208664	0.9686	0.0504
18	2.141304	19	2.1402246	1.0794	0.0504
19	2.372636	20	2.37144	1.196	0.0504

The electron wave functions, ψ , and electron density functions, $|\psi|^2$, for the ground state, 1st and 2nd excited states are shown in Figure 3.1.

(a) ground state, ψ

(b) ground state, $|\psi|^2$

(c) 1st excited state, ψ

(d) 1st excited state, $|\psi|^2$

(e) 2nd excited state, ψ

(f) 2nd excited state, $|\psi|^2$

Figure 3.1: The electron wave functions ψ and electron density functions $|\psi|^2$ for electrons confined in the 1D infinite well of width $L=30.76\text{nm}$.

3.3 2D-square quantum dots in infinite well

3.3.1 Energy levels, envelope functions and electron densities

In this section, the numerical finite element method (FEM) is used to simulate a two-dimension square quantum dot in an infinite well, and compare with energies of the analytical method [Pujari et al., 2008]. We consider the electron confinement in a square GaAs quantum dot of size 30.76 nm by 30.76 nm similar to Rasanen et al. [2003]. The governing equation is

$$\begin{cases} -\frac{\hbar^2}{2m_e^*} \nabla_e^2 \psi(r) + V_e(r) \psi(r) = \varepsilon \psi(r) \\ m_e^* = 0.067 m_e \\ V_e(r) = \begin{cases} 0 & 0 \leq x, y \leq L \\ \infty & \text{elsewhere} \end{cases} \end{cases} \quad (3.3)$$

where $\psi(r)$ is the electron envelop function in the radial direction, $\hbar$ the usual Planck constant, m_e^* the effective electron mass, $V_e(r)$ the electron confining potential, and ε the energy eigenvalues.

The analytical solution [Rasanen et al., 2003] is

$$E_{n_x, n_y} = \frac{1}{2} (n_x^2 + n_y^2) H_a^* \quad \begin{cases} n_x, n_y = 1, 2, 3, \dots \\ H_a^* = 11.8572 \text{ meV} \end{cases} \quad (3.4)$$

We present the results of the FEM simulation and analytical solution in Table 3.2. The differences in the energies are in the order of less than 1 meV (or percentage wise less than one percent). The analytical calculation give the exact solutions with the minimum energy states, and the variational method, such as FEM, will get better results towards the minimum energy states with more meshes. The differences between the analytical calculation and FEM increases with the higher excited states. The maximum difference at the 19th excited state is 0.21 meV or 0.14%.

Table 3.2: Comparison of FEM simulation results for a 2D-square quantum dot against analytical solutions for electrons confined in an infinite square well. The energy states for 20 states from the present FEM simulation and analytical results are compared.

State	FEM				Analytical		
	Energy (eV)	n_x	n_y	N	E_{n_x, n_y} (eV)	Differences (meV)	%
ground	0.011863	1	1	2	0.0118572	0.00580	0.049
1	0.029659	2	1	4	0.029643	0.01600	0.054
2	0.029659	1	2	6	0.029643	0.01600	0.054
3	0.047456	2	2	8	0.0474288	0.02720	0.057
4	0.059322	3	1	10	0.059286	0.03600	0.061
5	0.059322	1	3	12	0.059286	0.03600	0.061
6	0.077122	3	2	14	0.0770718	0.05020	0.065
7	0.077124	2	3	16	0.0770718	0.05220	0.068
8	0.100864	4	1	18	0.1007862	0.07780	0.077
9	0.100868	1	4	20	0.1007862	0.08180	0.081
10	0.106802	3	3	22	0.1067148	0.08720	0.082
11	0.118673	4	2	24	0.118572	0.10100	0.085
12	0.118677	2	4	26	0.118572	0.10500	0.088
13	0.148375	4	3	28	0.148215	0.16000	0.108
14	0.148383	3	4	30	0.148215	0.16800	0.113
15	0.154314	5	1	32	0.1541436	0.17040	0.110
16	0.154329	1	5	34	0.1541436	0.18540	0.120
17	0.172139	5	2	36	0.1719294	0.20960	0.122
18	0.172144	2	5	38	0.1719294	0.21460	0.125
19	0.189988	4	4	40	0.1897152	0.27280	0.144

Figure 3.2(a) shows the ground state energy probability density function $|\psi|^2$ which depicts the confined energy state of 0.011863 eV. The energy density is highest at the centre of the 2D square quantum dot and decays towards the edges. The energy envelop is bounded within the quantum dot because of the infinite well at the boundary between the quantum dot and the matrix. Figure 3.2(b) provides a 3D representation of the energy density surface contour for the ground state.

For a 2-dimensional square quantum dot, we expect energy degeneracies where $n_x = n_y$ such as the 1st and 2nd excited states, the 4th and 5th excited states, etc. However we would like to point out that the electron density degenerate states are not just spatially re-oriented along the x — y axes but totally different in density distribution, eg., the 4th and 5th energy density states shown in Figure 3.7 and Figure 3.8.

The electron energy density states, $|\psi|^2$, from the ground state to the 19th excited state and the electron energy density surface contours from the ground to the 19th excited state are given from Figure 3.2 to Figure 3.22. The electron ground state

has the 1S shape function similar to the real atom, and with excited states have analogical “spdf” shell profiles.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.2: The ground state energy density function $|\psi|^2$ for an electron in a 2D square with infinite well and the ground state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.3: The 1st excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 1st excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.4: The 2nd excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 2nd excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.5: The 3rd excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 3rd excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.6: The 3rd excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 3rd excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.7: The 4th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 4th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.8: The 5th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 5th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.9: The 6th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 6th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.10: The 7th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 7th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.11: The 8th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 8th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.12: The 9th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 9th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.13: The 10th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 10th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.14: The 11th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 11th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.15: The 12th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 12th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.16: The 13th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 13th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.17: The 14th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 14th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.18: The 15th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 15th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.19: The 16th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 16th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.20: The 17th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 17th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.21: The 18th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 18th excited state energy surface contour.

(a) density function $|\psi|^2$

(b) surface contour

Figure 3.22: The 19th excited state energy density function $|\psi|^2$ for a 2D square with infinite well and the 19th excited state energy surface contour.

3.4 Energy shells and Hund's rules

The quantum dot is called an artificial atom because it also has similar closed shell structures for its electrons that obey Hund's rules though the "magic numbers" are not the same as the real atom. For our simplified 2D-square quantum dot, we have obtained the energy levels for the first 20 energy states, see Table 3.2. We also show in Figure 3.23, the energies versus N as energy steps to determine the magic numbers for the closed shells. The closed shells for the 2D-square quantum dot in infinite well are at $N = 2, 6, 8, 12, 16, 20, 22, 26, 30, 34, 38$.

The first reported shell filling numbers were given by Knight et al. [1984] as $N = 2, 8, 20, 40, 58$ and 92. Barnett et al. [1999], Reimann and Manninen [2002], Ezaki et al. [1997] reported magic numbers for real 3D quantum dots at $N = 2, 6, 12, 20, 30, 42, 56, 72, 90, 110, \dots$ and half-filled at $N = 4, 9, 16, 25, 36, 49, \dots$. There are variations, such as Voon and Willatzen [2002] who used Hartree-Fock approximation and obtained $N = 2, 5, 8, 13, 19, 27, 34, 37$, and Aichinger and Rasanen [2005] who solved the Kohn-Sham equations using spin-density-functional theory (SDFT) to obtain $N = 2, 6, 12, 20$ for 2D quantum dots.

There are basically three Hund's rules:

1. The first rule states that, consistent with the Pauli principle, the state with the highest total spin (S) will have the lowest energy.
2. The second rule states that, for a given spin, the state with the highest total orbital angular momentum (L), consistent with the overall antisymmetization, will have the lowest energy.
3. The third rule states that if a subshell (n, l) is no more than half filled, then the lowest energy level has $J = |L - S|$; if it is more than half filled, then $J = L + S$ has the lowest energy.

The Hund's rules for quantum dots are currently still under intensive research under different applied external confinement potential (in 2DEG), external magnetic field, nano-indentation, etc.

Figure 3.23: The energies for the respective number of atoms, N , are given in Table 3.2. The plot shows the energies for different N . From the energy states, we derived the magic numbers, 2, 6, 8, 12, 16, 20, 22, 26, 30, 34, 38, of closed shells for the 2D-square quantum dots in infinite well. This is similar to Hund's rules for atomic shells.

3.5 3D self-assembled pyramidal InAs/GaAs quantum dot

We next simulate the 3D self-assembled quantum dot [Voss, 2006, Pryor et al., 1998, Gelbard and Malloy, 2001, Grundmann et al., 1995, Fonseca et al., 1998, Stier et al., 1999, Marzin and Bastard, 1994, Stoleru et al., 2002, Wang et al., 2009], and employed the same InAs/GaAs material parameters as Hwang et al. [2004], where the potential within the pyramidal quantum dot, $V_q=0\text{eV}$, and potential of the external matrix barrier, $V_m=0.77\text{eV}$, the effective electron mass, $m_e^*=0.024m_e$ for the quantum dot, $m_e^*=0.067m_e$ for the cuboid and m_e is the mass of the electron.

The structural set-up of the pyramidal quantum dot is given in Figure 3.24.

Figure 3.24: The structural set-up of a 3D pyramid, $12.4\text{nm}(b) \times 6.2\text{nm}(h)$, quantum dot in cuboid matrix ($24.8\text{nm} \times 24.8\text{nm} \times 18.6\text{nm}$). The material for the quantum dot is InAs and the cuboid matrix is GaAs.

The electron density, computed by squaring the eigenvectors, of the ground state, 1^{st} and 2^{nd} excited state energies are shown in Figure 3.25 and Figure 3.26, Figure 3.27 and Figure 3.28, and Figure 3.29 and Figure 3.30 respectively.

Figure 3.25: 3D-pyramid, 12.4nm(b) $\times$ 6.2nm(h) InAs/GaAs QD, ground state energy density $|\psi|^2$ for electron in finite well.

Figure 3.26: 3D-pyramid, 12.4nm(b) $\times$ 6.2nm(h) InAs/GaAs QD, ground state energy density $|\psi|^2$ for electron in finite well in the x-y plane.

Figure 3.27: 3D-pyramid, 12.4nm(b) $\times$ 6.2nm(h) InAs/GaAs QD, 1st excited state energy density $|\psi|^2$ for electron in finite well.

Figure 3.28: 3D-pyramid, 12.4nm(b) $\times$ 6.2nm(h) InAs/GaAs QD, 1st excited state energy density $|\psi|^2$ for electron in finite well in the x-y plane.

Figure 3.29: 3D-pyramid, 12.4nm(b) $\times$ 6.2nm(h) InAs/GaAs QD, 2nd excited state energy density $|\psi|^2$ for electron in finite well.

Figure 3.30: 3D-pyramid, 12.4nm(b) $\times$ 6.2nm(h) InAs/GaAs QD, 2nd excited state energy density $|\psi|^2$ for electron in finite well in the x-y plane.

The ground state, and the degenerate 1st and 2nd excited states are in good agreement with Hwang et al. [2004] constant effective mass model which was solved using the finite volume method (FVM). The results are tabulated in Table 3.3 for comparison.

Table 3.3: Comparison of present FEM simulation results for 3D-pyramid InAs-GaAs quantum dot with the finite volume numerical method. The energy states for ground, 1st and degenerate 2nd excited states are given (there are only three confined states). The differences are less than 1 meV.

	Present (eV)	Hwang et al. [2004] (eV)
Energy State	Energy (eV)	Energy (eV)
Ground	0.391114	0.3910
1st excited state	0.638053	0.6380
2nd excited state	0.638063	0.6380

3.6 3D CdS colloidal quantum dots

The single-particle finite well effective mass approximation (FWEMA) Schrödinger equation is discretized by the finite element method. We simulate the 3D CdS nanocrystals of radius, R , ranging from 0.5 nm to 24 nm.

With the FWEMA numerical simulation, we calculate $\Delta E_g = E_e + E_h$ where E_e is the electron ground energy and E_h is the hole ground energy. Both electron and hole energies are obtained separately using the finite element method where we discretized the single-particle (electron, hole) Schrödinger equation with quadratic Lagrangian elements on a tetrahedral grid. The quantum dots are approximated by an isotropic continuous medium with the wavefunction ψ vanishing at the outer edges of the matrix, and equal effective masses in the quantum dots and matrix,

$$\begin{aligned}
 & -\frac{\hbar^2}{2m_e^*} \nabla_e^2 \psi(r) - \frac{\hbar^2}{2m_h^*} \nabla_h^2 \psi(r) + V_e(r_e) \psi(r) + V_h(r_h) \psi(r) = E \psi(r) \\
 & \left\{ \begin{array}{l} m_e^* = 0.18m_e \\ m_h^* = 0.53m_e \\ \frac{m_i}{m_o} = 1 \\ V_e = V_h = 0 \\ V_{matrix} = 2.25 \text{ eV} \end{array} \right. \left\{ \begin{array}{l} i = e, h \\ o = \text{matrix} \end{array} \right. \quad (3.5)
 \end{aligned}$$

The above parameter values are taken from Marin et al. [1998] and Li et al. [2001b].

A detailed convergence study is carried out here to determine the number of finite elements required to generate mesh insensitive results. We selected the cases of CdS sample sizes of $R=0.5\text{nm}$ and $R=2.5\text{nm}$, which possess very strong quantum size effect.

For the case of $R=0.5\text{nm}$, convergence was achieved with about 30,000 elements, while for the case of $R=2.5\text{nm}$, 40,000 elements were required.

The representative results for ground state electron transition energies, ΔE_e , for $R=0.5\text{nm}$ and $R=2.5\text{nm}$ are given in Table 3.4 and Figure 3.31, and Table 3.5 and Figure 3.32, respectively.

Table 3.4: The electron ground state energies were simulated with gradually refined finite elements for radius $R=0.5\text{ nm}$.

No. of Elements	ΔE_e (eV)
895	2.249457
1512	2.247169
3989	2.245526
8199	2.243681
20903	2.243367
37006	2.243262
81157	2.243231

Figure 3.31: The FEM convergence plot for 0.5nm CdS nanocrystals.

Table 3.5: The electron ground state energies were simulated with coarse to fine finite elements for radius $R=2.5\text{nm}$.

No. of Elements	ΔE_e (eV)
978	0.272927
1540	0.271242
3471	0.268179
5705	0.266903
16128	0.265207
29724	0.26477
83223	0.26448

Figure 3.32: The FEM convergence plot for $R=2.5\text{nm}$ CdS nanocrystals.

For our subsequent simulations, we use elements numbering between 50,000 to 90,000. The results of the simulation for electron, hole and exciton (emission) energies are tabulated in Table 3.6. With the confinement energies from EMA, FWEMA and experiments, we calculate the effective volume and effective radius. The data for the FWEMA are given in Table 3.6.

Table 3.6: The electron, hole energies and ΔE_g of simulated CdS colloidal nanocrystals.

R (nm)	V (nm ³)	E_e (eV)	E_h (eV)	$\Delta E_g = E_e + E_h$ (eV)
0.5	0.52	2.24323	1.42245	3.66568
1	4.19	1.16021	0.50559	1.66580
1.5	14.14	0.62988	0.25201	0.88188
2	33.51	0.39076	0.15035	0.54112
2.5	65.45	0.26446	0.09970	0.36415
3	113.10	0.19183	0.07103	0.26286
3.5	179.59	0.14438	0.05313	0.19751
4	268.08	0.11353	0.04122	0.15475
4.5	381.70	0.09073	0.03289	0.12362
5	523.60	0.07445	0.02688	0.10133
6	904.78	0.05312	0.01866	0.07198
7	1436.76	0.03948	0.01395	0.05342
8	2144.66	0.03053	0.01073	0.04125
9	3053.63	0.02430	0.00851	0.03281
10	4188.79	0.01983	0.00692	0.02676
12	7238.23	0.01396	0.00485	0.01880
14	11494.04	0.01031	0.00357	0.01388
16	17157.29	0.00795	0.00274	0.0107
18	24429.03	0.00632	0.00217	0.00849
21	38792.39	0.00461	0.00159	0.00620

The present simulated energy values are compared with the data from Rossetti et al. [1984] and tabulated in Table 3.7. The data came in the form of absorption threshold in wavelength unit of nm. We used the Planck's formula $E = \frac{hc}{\lambda_e}$ to convert wavelength to their equivalent energies (E_g). The change in band gap is computed with $\Delta E_g = E_g - E_g^{bulk}$ where E_g^{bulk} is taken, for convenience, to be 2.5303 eV so that $\Delta E_g^{bulk} = 0$. The energy values are comparable to Kayanuma [1988] prediction model and the experimental data of Ekimov and Onushchenko [1982].

Table 3.7: Data obtained from Rossetti et al. [1984]. The energy was converted from the threshold wavelength by us using Planck's formula, $E = \frac{hc}{\lambda_e}$.

R (nm)	threshold (nm)	Calculated E_g (eV)	ΔE_g (eV)
Bulk	490	2.5303	0
3.75	478	2.5938	0.0635
3.3	471	2.6324	0.1021
2.85	461	2.6895	0.1592
2.4	444	2.7924	0.2621
1.95	416	2.9804	0.4501
1.5	367	3.3783	0.8480
1.05	286	4.3351	1.8048

The simulated FEM results are given in Table 3.6 and corresponding experimental data in Table 3.7. The exciton energy is $E_{electron} + E_{hole} + E_g^{bulk}$ where E_g^{bulk} is taken as 2.5eV. They are plotted in Figure 3.33 for comparison.

Figure 3.33: Curve fitting of our numerical simulated data and those from Rossetti et al. [1984].

The match between the simulated data and the data from Rossetti et al. [1984] is good. This validates our single-particle EMA approximation and our FEM model. At sizes between 3—12 nm our simulated energies are slightly higher and this could be due to the neglect of the (negative) Coulomb interaction term in the Hamiltonian.

Figure 3.34 and Figure 3.35 show the electron density for 3D nanocrystals of $R=0.5\text{nm}$ and $R=2.5\text{nm}$, respectively. For the case of $R=0.5\text{nm}$, the electron penetrated out of the quantum dot due to very high QSE overcoming the finite well potential of 2.25eV. The ground state energy of about 2.24eV is just slightly below the confinement limit. For the case of $R=2.5\text{nm}$, the electron is confined within the quantum dot.

Figure 3.34: The ground state electron density, $|\psi|^2$, for a 3D $R=0.5\text{nm}$ CdS nanocrystal.

Figure 3.35: The ground state electron density, $|\psi|^2$, for a 3D $R=2.5\text{nm}$ CdS nanocrystal.

Next, the larger quantum dot of $R=21\text{nm}$ is simulated and the results of the 1st 20 energy states for electron and hole are given in Table 3.8. The electron and hole ground states are shown in Figure 3.36 and Figure 3.37 respectively. Even though the transition energy of the hole is lower (due to its heavier effective mass), the hole density, $|\psi|^2$, fill the space within the quantum dot. The intensity of the electron density is higher than the hole.

Table 3.8: The present FEM simulation results for 3D-sphere CdS quantum dot confined in an finite well. The energy states for 20 states of the electrons and holes are given. The electron and hole systems are simulated separately with 189,857 and 142,878 elements respectively.

Energy State	Electron (eV)	Hole (eV)	atomic-like shell
ground	0.004614	0.001591	1s
1	0.009437	0.003253	2p
2	0.00944	0.003254	2p
3	0.009441	0.003255	2p
4	0.015525	0.005352	3d
5	0.015529	0.005353	3d
6	0.01553	0.005354	3d
7	0.015531	0.005355	3d
8	0.015533	0.005355	3d
9	0.018457	0.006363	2s
10	0.022824	0.007869	4f
11	0.022828	0.00787	4f
12	0.022828	0.00787	4f
13	0.022831	0.007872	4f
14	0.022833	0.007872	4f
15	0.022833	0.007873	4f
16	0.022834	0.007874	4f
17	0.027897	0.009618	3p
18	0.027903	0.009622	3p
19	0.027907	0.009623	3p

Figure 3.36: The ground electron density, $|\psi|^2$, for a three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.37: The ground hole density, $|\psi|^2$, for a three-dimensional $R=21\text{nm}$ CdS nanocrystal.

The 1st to 19th electron excited states of the large CdS nanocrystal with $R=21\text{nm}$ are shown from Figure 3.38 to Figure 3.56. The electron density, $|\psi|^2(\equiv \text{abs}(u)^2)$ are presented with slice/intersection through the $x-y$, $y-z$, $x-z$ planes, and the isosurface plots.

Figure 3.38: The 1st excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.39: The 2nd excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.40: The 3rd excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.41: The 4th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.42: The 5th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.43: The 6th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.44: The 7th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.45: The 8th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.46: The 9th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.47: The 10th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.48: The 11th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.49: The 12th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.50: The 13th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.51: The 14th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.52: The 15th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.53: The 16th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.54: The 17th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.55: The 18th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

Figure 3.56: The 19th excited state with electron density, $|\psi|^2$, for a large three-dimensional $R=21\text{nm}$ CdS nanocrystal.

The energy levels for the hole are significantly lesser than the electron, however, their “atomic-like” shells are similar. The ground and 9th excited states are 3D symmetrical have the “S”-like envelop functions. The 2nd to 3rd excited states have the “2p” shells, 4th to 8th excited states have the “3d” shells, 10th to 16th excited states have the “4f” shells and 17th to 19th excited states have the “3p” shells.

3.7 Concluding remarks

The 2D-square quantum dots in infinite well, the 3D pyramidal InAs/GaAs self-assembled quantum dots, and the 3D colloidal (spherical) CdS quantum dots have been numerically simulated using the FEM. The transition energies of the 2D-square quantum dots have been verified with the analytical calculations, the 3D pyramidal quantum dots compared with the finite volume method and the 3D colloidal CdS quantum dots validated with known experimental results. Our numerical simulation results are in excellent agreement.

The computational modeling tools of the finite well effective mass approximation (FWEMA) and finite element method (FEM) have thus been established to be suitable for numerical simulation of quantum dots.

Chapter 4

Interfacial Capping Layer for InAs/GaAs SAQDs

Quantum dots exhibit interesting structural and electronic properties due to the quantum size effect at nanoscale. They are used as bio-tags to emit different color light with different dot sizes, and quantum dots are currently extensively studied for application as quantum devices taking advantage of the “artificial atom” properties such as their discrete energies, electron spins and quantum transport energies. Quantum dots generally exist as spheroidal nanoclusters in suspension, and pyramidal or conical heterostructures on substrate. The self-assembled semiconductor quantum dots are grown on the wetting layer of a few monolayer thickness and subsequently capped with a strain-reduction layer covering the dots to stabilize them. We study the indium arsenide/gallium arsenide self-assembled quantum dots modeled with a wetting layer between the quantum dot and substrate, and the strain-reducing capping layer above the quantum dot. We introduce a new model with an interfacial layer between the quantum dot and the capping layer and investigate the effective mechanical and electronic properties using the finite element method and deformation potential theory. The modified strains along the [001] direction through the center to the tip of the pyramid of the quantum dots are obtained for different elastic modulus of the interfacial capping layer. We evaluate that the interfacial capping layer with higher elastic modulus correctly depicts the ground state band gap energy.

4.1 Introduction

Quantum dots generally exist as nanoclusters in suspension using chemical process, or grown by Stranski-Krastanov (SK) process embedded in semiconductor matrix using molecular beam epitaxy (MBE) or various vapor/particle deposition

methods. Quantum dots in the size range of 2–6 nm have been extensively used in biology for tagging to trace the spatial movement of macro-molecules [Jamieson et al., 2007] as different sizes of quantum dots emit lights of different color when illuminated. Quantum dots have been used to produce white light [Joswig et al., 2000], something that has not been done with single LED diode. It has also been applied in solar cells [Gupta et al., 2009] and quantum-dot lasers [Sugawara et al., 2007]. There are extensive research to apply quantum dots to quantum computing using quantum spin, quantum transport, etc [Burkard et al., 2000].

The physical and electronic properties of quantum dots at nanoscale deviate from the bulk. Due to the quantum size effect (QSE) the ground state energy of carriers (electron or hole) and the spacing of the energy levels increase as the size decreases at nanoscale. The carrier confinement in quantum dots has been studied by Brus [1983, 1984b], Ekardt [1985] and Kayanuma [1986, 1988] and they have defined a simple scaling law to analyze the spherical quantum dot nanocrystal within a single-band effective mass approximation (EMA),

$$E_g(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786e^2}{\epsilon_r R} - 0.284 E_{R_y^*} \quad (4.1)$$

where $E_g(R)$ is the quantum dot band gap as a function of radius R , $E_g(\infty)$ the bulk band gap, $\hbar$ the usual Planck's constant divided by 2π , $E_{R_y^*}$ the constant effective Rydberg energy for bulk semiconductor, and μ the reduced mass. The second term of Equation (4.1) is the kinetic energy, the third term is the Coulomb energy, while the last term is the electron-hole interaction. The EMA assumes an infinite barrier and a constant effective mass in the nanocrystal. The equation exemplifies the well-known quantum confinement induced scaling of $1/R^2$ and also the presence of a $-1/R$ scaling due to electrostatic effects. In general the experimental evidence typically indicates a $1/R^n$ scaling with $1 < n < 2$. The electrostatic interactions ($-1/R$ scaling) and other physical causes are responsible for the deviation from the idealized quantum confinement of $n = 2$.

The self-assembled quantum dots (SAQDs) are formed through the Stranski-Krastanov growth mode [Chia et al., 2007, Kim et al., 1998, Pohl et al., 2006] by strained layer epitaxy of InAs on GaAs near the critical value for the onset of the 2D–3D transition due to mismatched lattice constants. At the initial state, the system consists of flat, 1 monolayer (ML) high islands on the wetting layer (WL) with a broad distribution in base lengths. As 2 ML high islands form, the barrier strength increases, hindering further island growth in base length. Further growth will then occur via monolayer nucleation on the top facet. The island base then remains constant and the height increases by one monolayer after another. The

energetics of the growth of every subsequent atomic layer atop a given pyramidal quantum dot is described by a change of the Gibbs free energy. After the formation of the SAQD, a capping layer of a few to tens of nanometers, is applied to stabilize the quantum dots. At the interfacial zone of 3–4 atomic layers, where the atoms have different energy than their bulk counterparts, Dingreville and Qu [2009] observed that the atomic level stiffness/compliance tensor is no longer positive definite for some atoms near the interface.

In the semiconductor SAQD, the strain in the quantum dot and surrounding matrix affects the band edge offsets of the conduction band (CB) and valence band (VB). Typically strain is estimated using classical/continuum elasticity and then coupled to a suitable band structure calculation approach. At the size scale of a few nanometers, the elastic relaxation is size dependent [Broughton and Meli, 1997, Li et al., 2003, Sharma and Ganti, 2002, 2004, Peng et al., 2005]. The physical cause of this size-dependency of strain is due to the involvement of surface or interface energies at the nanoscale due to a large surface-to-volume ratio. The transition from atomistic scale to the continuum limit has also been reported by Dingreville and Qu [2009] in their multi-scale evaluation.

We introduce, within the elasticity model, a one-monolayer (ML), which is the limit of classical elasticity [Brandt et al., 1992, Bernard and Zunger, 1994, Hospodkova et al., 2008], interfacial capping layer between the final quantum dot and the capping layer, in the next section. We also set up the model of pyramidal InAs/GaAs SAQD for numerical simulation using the finite element method (FEM). Then we explain the deformation potential theory to calculate strain-induced band offsets, and the effective mass approximation (EMA) method to calculate the confinement energies for electron and hole. The results of the numerical simulations are then given, and finally we discuss the effects of the elastic constant of the interfacial capping layer.

4.2 Interfacial capping layer (ICL) model

The classical elasticity theory is intrinsically size independent and the elastic field is scale-invariant for any shape and size of the quantum dot which is uncapped and neglecting the wetting layer. Since the wetting layer has a fixed thickness, regardless of the size of the island, this breaks the scale-invariant condition, making the elastic energy density size-dependent. Thus the main contribution to the size-dependent elastic field for the strained self-assembled quantum dot is the presence of the capping layer. In the capping process, due to the different materials used, there

will be a transition interfacial layer between the quantum dot and capping layer and this has not been modeled specifically in classical/continuum elasticity models. The present work considers a mono-layer (0.3 nm) interfacial capping layer (ICL) of the self-assembled pyramidal InAs/GaAs quantum dot of 22 nm square base-length and height 3nm embedded in a $60 \times 60 \times 60$ nm cuboid, as shown in Figure 4.1. Due to dual symmetry, we can reduce the computational effort with a quarter size model.

The WL is layered on the GaAs substrate. The pyramidal quantum dot is grown on the WL (0.3 nm), and the one monolayer ICL of 0.3 nm is the interface between the InAs QD and the GaAs capping layer. The pyramidal quantum dot has a square base of 22 nm and height of 3 nm. The InAs QD is embedded in a cuboid with side length of 60 nm. For the FEM simulation of the mechanical properties, they are meshed with Solid98 elements which support temperature degree-of-freedom (DOF).

(a) Quantum dot with WL and ICL (the surrounding matrix not shown)

(b) A quarter quantum dot with WL, ICL and matrix

Figure 4.1: The ICL FEM model.

4.3 Material and methods

We present an investigation of the strain distribution in and around the self-organized InAs/GaAs quantum dot, whose pyramidal shape has been evidenced by high-resolution transmission electron microscope (TEM) and atomic force microscope (AFM). Numerical results for the strain distribution and energies of carriers (electron, hole) are obtained by minimizing the total energy of the quantum dot, wetting layer, interfacial capping layer and the surrounding matrix/barrier.

The pyramidal InAs/GaAs has a lattice mismatch strain

$$\epsilon_{ij}^m = \epsilon^m \delta_{ij} \quad (4.2a)$$

$$\epsilon^m = \frac{a_{matrix} - a_{QD}}{a_{matrix}} = -0.067 \quad (4.2b)$$

where $a_{QD} = 0.605830\text{nm}$ is the lattice constant of the InAs quantum dot and $a_{matrix} = 0.565325\text{nm}$ is the lattice constant of the GaAs matrix.

The usual method [Ellaway and Faux, 2002] is to take the InAs QD and compress it uniformly by about 6.7% in each direction so that it has the same lattice constant as GaAs. It is then placed in a hole of exactly the right size, so that the InAs and GaAs crystals are coherent, and the uniform compression is then removed. The quantum dot relaxes part of its strain and the surrounding matrix becomes strained. The knowledge of the quantum dot induced strain distribution is required to calculate the electronic and optical properties.

The misfit is modeled as a thermoelasticity problem [Benabbas et al., 1996]. The strain is introduced by setting the thermal expansion coefficient of the island and the substrate to 0.067 K^{-1} and 0, respectively, and raising the temperature by 1 K. The thermal strain is defined as,

$$\epsilon_T = a_T \Delta T \quad (4.3)$$

where a_T is the thermal expansion coefficient and T is the temperature.

We simulate four types of quantum dots. The Type0 quantum dot is the usual model without the ICL. The Type1 quantum dot assumes the intermediate material properties of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ in the ICL, while the Type2 and Type3 quantum dots assume, arbitrarily, the Young's modulus of $2 \times 10^{11}\text{ N/m}$ and $2 \times 10^{10}\text{ N/m}$ respectively. The normal displacement and the temperature of the outer matrix boundaries are taken to be zero in the normal direction and 0 K, respectively. The quantum dot has a square base of 22 nm length with height of 3 nm. The wetting layer and interfacial capping layer are one monolayer thick (0.3 nm). The simulation parameters [Liu and Quek, 2002] are given in Table 4.1.

4.4 Theories and calculation

In this work, we use the Eshelby's inclusion theory and the finite element method (FEM) [Barnett et al., 1999, Liu and Quek, 2002, Hwang et al., 2004, Ngo et al., 2009] to calculate the strains in the pyramidal InAs-GaAs quantum dot system

Table 4.1: The material parameters for simulation of the pyramidal InAs/GaAs QDs taken from Liu and Quek [2002].

	Matrix	WL	QD	ICL Type1	ICL Type2	ICL Type3
Density (kg/m ³)	5320	5680	5680	5500	5500	5500
Young's Modulus, ($\times 10^{10}$ Nm)	8.69	5.14	5.14	6.87	20	2
Poisson ratio, ν	0.31	0.35	0.35	0.33	0.33	0.33
Heat capacity (J/kg°C)	330	250	250	290	290	290
Thermal conductivity (W/m°C)	550	270	270	410	410	410
Thermal expansion (nm/°C)	0	0.067	0.067	0	0	0
Thermal load, °C	T	T	1	T	T	T
Initial temperature, K	0	0	0	0	0	0

[Jiang and Singh, 1997, Andreev et al., 1999, Stier et al., 1999, Wang et al., 2000b, Stoleru et al., 2002, He et al., 2004, Wang et al., 2006, Lin et al., 2007, Gong et al., 2008, Richter et al., 2008], and the deformation potential/inclusion theory to obtain the strained-induced confinement potential, and then investigate the carrier confinement energies of the electron and hole using the finite well effective mass approximation (FWEMA) theory.

The strains follow from substitution of the stresses into Hookes law

$$\epsilon_{ij} = \frac{1}{E} [(1 + \nu)\sigma_{ij} - \delta_{ij}\nu\sigma_{kk}] \quad (4.4)$$

where $\epsilon_{ij} = \partial u_i / \partial_j$ denotes the strain and u is the displacement vector field, E the Young's modulus and ν the Poisson ratio. Thus, for the hydrostatic strain, ϵ_h , and the biaxial strain, ϵ_b [Williamson and Zunger, 1999, Pearson and Faux, 2000, Pryor et al., 1998],

$$\begin{aligned} \epsilon_h &= \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \\ \epsilon_b &= \epsilon_{zz} - \frac{1}{2}(\epsilon_{xx} + \epsilon_{yy}) \end{aligned} \quad (4.5)$$

where ϵ_{xx} , ϵ_{yy} , and ϵ_{zz} are the strains in the x -axis, y -axis and z -axis respectively.

4.4.1 Deformation potential theory

With the strains, we can calculate the strain-modified confinement potentials along the [001] direction through the pyramidal tip. The shear strains (off-diagonal terms of the strain tensor) are zero and $\epsilon_{xx} = \epsilon_{yy}$, thus the effective confinement potentials can be simplified as

$$E_c(r) = E_c^o(r) + a_c(r)\epsilon_h \quad (4.6)$$

where $E_c(r)$ is the conduction-band state and $E_c^o(r)$ is the energy of the conduction-band minimum of the bulk material at r , and a_c is the deformation potential of the conduction band under hydrostatic deformation.

The effect of the strain profiles on the electronic structure of the dots can be qualitatively understood from the strain-modified band offsets [Grundmann et al., 1995, Pryor et al., 1998, Williamson and Zunger, 1999]. They can be approximately calculated by coupling the electron and hole band edges to their deformation potentials. The electron band edge E_c couples only to the sum of the diagonal strain components, $\delta E_c = -a_c(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})$, where a_c is the deformation potential of the conduction band under hydrostatic deformation. The strained-induced potential is given as

$$V^{\alpha\beta}(\vec{r}) = V_{band}^{\alpha\beta}(\vec{r}) + V_{strain}^{\alpha\beta}(\vec{r}) \quad (4.7)$$

Along the [001] direction (z axis) through the pyramidal tip, the shear strains (off-diagonal terms of the strain tensor) are zero and $\epsilon_{xx} = \epsilon_{yy}$, and the effective confinement potentials of the heavy- and light-hole band edges, E_{hh} and E_{lh} , couple to the individual strain components according to

$$E_{hh} = E_v^o + a_v\epsilon_h + \frac{1}{3}(\Delta^{SO} + \Delta^S) \quad (4.8a)$$

$$E_{lh} = E_v^o + a_v\epsilon_h - \frac{1}{6}(\Delta^{SO} + \Delta^S) + \frac{1}{2}\sqrt{(\Delta^{SO} + \Delta^S)^2 - \frac{8}{3}\Delta^{SO}\Delta^S} \quad (4.8b)$$

$$\Delta^S = -3b\epsilon_b = -3b[\epsilon_{zz} - (\epsilon_{xx} + \epsilon_{yy})/2] \quad (4.8c)$$

where Δ^{SO} is the spin-orbit splitting, Δ^S the crystal field splitting, a_v the hydrostatic deformation of the valence states and b the uniaxial deformation potential. The biaxial strain splits the heavy hole (hh) and light hole (lh) bands in addition to shifting the valence band maximum (VBM).

4.4.2 Effective mass approximation theory

The basis equation in the nanoscale is the Schrödinger (quantum mechanics) wave function equation, $H\Psi = E\Psi$, where H is the Hamiltonian, $\Psi(r_1, r_2, \dots, r_N)$ is the wave function, E is the eigen-energies and r_n is the spatial dimensions. Further simplification assumes the nuclei to be static with electrons moving in the effective potential field, $H = -\frac{\hbar^2}{2}\nabla_r \cdot \left(\frac{1}{m(r)}\nabla_r\right) + V(r)$, where m_r is the spatial-dependent

effective mass of electron (hole) and $V(r)$ is the field potential as a function of radius r .

In the pyramidal SAQD, the smallest axial component is the major determinant of the confinement energies. In our pyramidal quantum dot (QD), the axial component from the base to the tip with a finite well width, is 3 nm. We use the average band edges of the conduction and valence bands and determine the well depth from the lower/shallower edge of the QD/WL or QD/ICL interfaces, averaging over 1 nm at the edges to negate the sharp peaks.

We use the finite depth/width square well EMA (FWEMA) method [Pellegrini et al., 2005] and employ the numerical finite element method (FEM) to solve the following Schrödinger equation

$$-\frac{\hbar^2}{2m_e^*}\nabla_e^2\psi(r) - \frac{\hbar^2}{2m_h^*}\nabla_h^2\psi(r) + V_e(r_e)\psi(r) + V_h(r_h)\psi(r) = E\psi(r) \quad (4.9a)$$

$$V_e = V_h = \begin{cases} 0 & \text{inside QD} \\ V_o & \text{outside QD} \end{cases} \quad (4.9b)$$

where r_e and r_h are the electron and hole position, respectively, relative to the center of the quantum dot, and V_e and V_h are the barrier heights of the confining potential for the electron and hole respectively. The effective masses of electron and hole are correspondingly $(0.024m_o, 0.067m_o)$ and $(0.4m_o, 0.5m_o)$ for InAs and GaAs respectively. The V_o for electron ($V_e^{barrier}$) and hole ($V_h^{barrier}$) are given in Table 4.3.

4.4.3 Finite element method

We first examined the strain profiles for the resulting strain-modified band offsets, and then the detailed electronic eigenstates of the strained quantum dots.

For the strain profiles, the constitutive equation is represented by the algebraic equation for mechanical displacements, $Ku = f$, where the K , u , and f represent stiffness matrix, displacement matrix, and force matrices, respectively. The u_{xx} and u_{zz} are the displacements. In the FEM, the displacement vector $\mathbf{u}(x, y, z)$ is interpolated using shape functions $\mathbf{u} = \mathbf{N}\mathbf{u}_e$, where the nodal displacement vector $\mathbf{u}_e$ (of our three dimensional hexahedral element) is given by $\mathbf{u}^T = \{\mathbf{u}_{e1} \ \mathbf{u}_{e2} \ \mathbf{u}_{e3} \ \mathbf{u}_{e4} \ \mathbf{u}_{e5} \ \mathbf{u}_{e6} \ \mathbf{u}_{e7} \ \mathbf{u}_{e8}\}$. The interpolation shape function matrix is given by $\mathbf{N} = \{\mathbf{N}_1 \ \mathbf{N}_2 \ \mathbf{N}_3 \ \mathbf{N}_4 \ \mathbf{N}_5 \ \mathbf{N}_6 \ \mathbf{N}_7 \ \mathbf{N}_8\}$. The matrix equations for all the elements are assembled to give $\mathbf{K}\mathbf{u} = \mathbf{f}$, where $\mathbf{K}$ is now the global stiffness matrix, $\mathbf{u}$ is the global displacement vector, and $\mathbf{f}$ is the global force vector. The equations

can then be solved to obtain the global displacements and hence the strain and stress in the model. The detailed formulation of the finite element equations can be found in most finite element literature.

The electronic energy levels in the dots are calculated by solving the three-dimensional effective mass Schrödinger equation. The carrier confinement potential in this equation is modified by the strain distribution calculated earlier. We used the FEM, in which the equation is discretized via tetrahedral solid elements. The eigenstates of the single-particle Schrödinger equation is represented by the algebraic equation $KU = \lambda_i MU$, where K and U represent the Hamiltonian, H , and wave function, ψ , respectively, and λ_i are the eigenenergies. M is a scalar.

We solved the algebraic eigenvalue problem $KU = \lambda_i MU$ by determining the ψ_i and λ_i as approximations to U and λ using the Arnoldi algorithm applied to the shifted and inverted matrix iteratively until all the eigenvalues in the user-specified interval are found. For the electronic properties, both electron and hole energies are simulated separately [Laheld and Einevoll, 1997] using the finite element method where we discretized the single-particle (electron, hole) Schrödinger equation with quadratic Lagrangian elements on a tetrahedral grid. Convergence studies were carried out to ensure that the results are grid insensitive. The quantum dots are approximated by an isotropic continuous medium and the wave function ψ vanish at the outer edges of the matrix, and equal effective masses of the electron and hole in both the quantum dots and matrix.

4.5 Results

4.5.1 Displacement profiles

The initial temperature of the quantum dot, wetting layer, interfacial capping layer and matrix are set at 0 K. The temperature of the quantum dot is raised by 1°C. The quantum dot and wetting layer are expand with an expansion coefficient of 0.067/C. The displacements along the z -axis from the base centre to the tip of the pyramid quantum dot are given in Figure 4.2. The displacements in the x -axis and y -axis are effectively zero, due to symmetry boundary constraints, compared to that of the z -axis. The displacements in the z -axis are due to thermal expansion in the quantum dot and the wetting layer.

Figure 4.2: u_{xx} (u_{yy}) and u_{zz} distribution in the Type0 InAs/GaAs quantum dot along the z -axis [001] through the base to tip of the pyramidal QD.

4.5.2 Strain profiles

The strain is determined by minimizing the elastic energy. The quantum dots are mainly under compressive strains in the x - and y -directions, as can be noted in Figure 4.3, due to the lattice mismatch of -0.067. The Type3 quantum dot has the highest tensile u_{xx} at the tip. This is due to the “softer” elastic modulus of the Type3 interfacial capping layer. The compressive strains are greatest at the base/wetting layer interface which is consistent with the geometry of the pyramidal quantum dot, with the highest tensile strain at the tip.

Figure 4.3: u_{xx} along base to tip of InAs/GaAs quantum dots. Due to symmetry the y -strains is the same as the x -strains.

From Figure 4.4, we can see that the u_{zz} in the quantum dots are mainly tensile

due to dilational strains. The Type3 quantum dot has the highest compressive u_{zz} strains at the tip. The compressive strains at the interface between the quantum dot and interfacial capping layer of the Type3 quantum dot are excessive and deviates significantly from those of the Type1, Type0 and Type2 quantum dots, and is therefore not a suitable candidate for the interfacial capping layer.

Figure 4.4: u_{zz} along base to tip of InAs/GaAs quantum dots.

The hydrostatic strains, ϵ_h , are isotopic in the quantum dots. The compressive dilational strains in the quantum dot are relatively constant except at the tip, and basically zero in the matrix as shown in Figure 4.5.

Figure 4.5: Hydrostatic strains, ϵ_h , along base to tip of InAs/GaAs quantum dots. The hydrostatic strains of the QDs are relatively constant and therefore isotopic within the dots.

The biaxial strains, ϵ_b , are mainly tensile in the quantum dots as shown in Figure 4.6 and compressive at the tip. The Type3 quantum dot has the highest compressive

biaxial strain.

Figure 4.6: Biaxial strains, ϵ_b , along base to tip of InAs/GaAs quantum dots. The biaxial strains are mainly tensile in the QDs and compressive at the tips.

4.5.3 Band gap offsets, electron and hole confinement energies

The band gap offsets are calculated using the strained-induced potential based on deformation potential theory. The InAs and GaAs parameters are taken from Pryor et al. [1998] and shown in Table 4.2. The band gaps of the conduction band minimum (CBM) and valence band maximum (VBM) are given in Figure 4.7.

Table 4.2: InAs and GaAs parameters. All units in eV.

	Substrate, ICL, CL (GaAs)	QD, WL (InAs)
a_c	-8.33	-6.08
a_v	1.16	1
b	-1.6	-1.8
E_c^o	1.52	0.66
E_v^o	0	0.25
Δ^{SO}	0.34	0.38

Figure 4.7: The strain-modified conduction (electron) and valence band (heavy-hole, light-hole) edges of InAs/GaAs quantum dots for Type0, Type1, Type2 and Type3 interfacial capping layers.

Using the band gap profiles, the mean values of the conduction band offset of electron, V_c , the valence bands of the heavy hole, V_{hh} , and the light hole, V_{lh} , along the z -axis from the base to the tip of the quantum dots are calculated. We determine the confinement potential, $V_e^{barrier}$ from V_c to the barrier height (base or the tip whichever is lower), and likewise from V_{hh} to $V_{hh}^{barrier}$, and V_{lh} to $V_{lh}^{barrier}$. These strain-induced band gaps are given in Table 4.3.

From the finite barrier confinement potentials calculated from the band diagrams,

we use the finite element method to solve Equation (7.6a) to obtain the confinement energies of the electrons and holes. The results are tabulated in Table 4.3. A graphical representation of the carrier confinement energies for Type0 quantum dot, for example, is given in Figure 4.8. The E_e (electron ground state) and E_{hh} (heavy-hole ground state) are the confinement energies for electron and heavy-hole respectively. The shape profiles are similar for the other quantum dot types, and their values are given in Table 4.3. The E_{hh} are consistent for all quantum dots while there are significant differences in the E_e . The E_g is the fundamental optical transition and we obtained 1.106 eV, 1.117 eV, 1.096 eV and 1.150 eV respectively for Type0, Type1, Type2 and Type3 quantum dots. Both Type1 and Type3 quantum dots have E_g higher than the reference Type0 quantum dot (without interfacial capping layer), while Type2 quantum dot is lower.

Table 4.3: Present results for Type0 (without ICL), Type1, Type2 and Type3 quantum dots. V_e^{QD} and V_h^{QD} are the confinement potential of electron and hole, respectively, in the quantum dots, and $V_e^{barrier}$ and $V_h^{barrier}$ are the confinement potential of electron and hole, respectively, in the matrix/barrier. All units are in eV.

Quantum Dot	Type 0	Type 1	Type 2	Type 3
V_c (mean)	1.123	1.115	1.139	1.088
V_{hh} (mean)	0.442	0.437	0.439	0.448
V_{lh} (mean)	0.277	0.281	0.274	0.283
$V_c - V_{hh}$	0.681	0.677	0.700	0.640
$V_c - V_{lh}$	0.846	0.834	0.865	0.805
$V_e^{barrier}$	0.453	0.487	0.398	0.642
$V_{hh}^{barrier}$	0.335	0.322	0.325	0.338
E_e	0.338	0.354	0.309	0.422
E_{hh}	0.087	0.086	0.087	0.088
E_g	1.106	1.117	1.096	1.150

Figure 4.8: E_g , E_e and E_{hh} confinement energies of Type0 InAs/GaAs quantum dot in a finite well.

4.6 Concluding remarks

An intermixing layer that exist between the quantum dot and the capping layer has been modeled as a mono-layer interfacial capping layer. This interface has been ignored in classical or continuum model as it is deemed to have a negligible effect or has been factored with the morphological shape changes in the quantum dots. This can lead to inaccuracies. In the microscopic scale, the Vegard's law is used to determine the intermediate property at the interface with a_f is $a_f = xa_{InAs} + (1 - x)a_{GaAs}$. The strain profiles of the Type3 quantum dot deviates significantly from known results and therefore is not a right interfacial capping layer candidate. The Type2 quantum dot is favored as it gives a lower ground state energy, E_g , which is expected from strain-reducing effect of the interfacial capping layer and capping layer. At nanoscale, based on our results, the Young's modulus with higher value is a better fit for the strained quantum dot where we obtained a band gap of 1.096 eV for the 22×22 nm square-base, height 3 nm pyramidal quantum dot – a difference of 10 meV from the Type0 quantum dot. We expect the difference to narrow for a more realistic 2–3 monolayer interfacial capping layer. Zhang and Sharma [2005] reported that the effective bulk and shear modulus are higher in nano-inhomogeneity and Sharma and Ganti [2002] showed clearly that the interfacial effects can add a substantial correction to the elastic state, especially at smaller sizes, and the corrections due to interfacial effects are comparable to both anisotropic effects and strain-dependent modulus effect.

In the capping process, there exist a transitional layer between the quantum

dot and the strain reducing layer, due to difference in material properties. This layer is not modeled specifically for current classical/continuum elasticity models. We have introduced an arbitrary one monolayer thickness interfacial capping layer between the quantum dot and the capping layer of the self-assembled quantum dot to determine the effective elastic modulus. The strains profiles, band gap offsets, confinement potentials, and confinement energies of electron and hole thus obtained demonstrated that the Type2 quantum dot, where a higher Young's modulus of 2×10^{11} Nm is favored as it reduces the ground band gap energies, as required of the strain-reducing interfacial capping layer and capping layers layer.

Chapter 5

Band Gap Energy and Size N

The band gap energy, E_g , of quantum dots, assuming an infinite barrier, has been expressed analytically by Brus [1984a], Kayanuma [1988] as $E_g = E_g^{bulk} + \frac{\hbar^2}{2\mu} \left(\frac{\pi}{R}\right)^2 - 1.786 \frac{e^2}{\epsilon R} - 0.248 E_{Ry}^*$. The band gap scales to R^{-2} with size. Another band gap energy and size relation that is used to fit the experimental data is $E_g = E_g^{bulk} + E_f/N^\beta$, with energy shift $\Delta E_g = E_f/N^\beta$. The band gap scales with size $N^{-\beta}$ where N is the number of atoms and the exponent β generally lies between 1/3 and 2/3. Other known band gap energy shift and size relations are given in terms of radius R , diameter d and volume V_o .

A “core-shell” model was developed to investigate the electronic size of the transition energy of the exciton (electron-hole quasi-particle) confined within the quantum dot. In this study, we examine the metallic gold (Au), semiconductor indium phosphate (InP) and semiconductor cadmium selenide (CdSe) quantum dots. The transition energy is expressed as $\Delta E_g = E_f(1 - 3(a_o^3/N_{cell})tN^{-1/3} + 3(a_o^3/N_{cell})^2t^2N^{-2/3} - (a_o^3/N_{cell})^3t^3N^{-1})$, where E_f is the Fermi energy. The results show that the core electronic size, depicted as volume $(d-t)^3$, to be confined within the physical volume. The equivalent radius, $(d-t)/2$, is different from the bulk effective exciton radius, a_B^* , however, they are of the same order of magnitude.

5.1 Introduction

It is well known that the transition energy, ΔE_g , is inversely proportional to size (d , V or N) such that $\Delta E_g \propto d^{-\alpha}, V^{-\gamma}, N^{-\beta}$. The quantum confinement energies are size, shape and material-dependent [Maksimenko et al., 2001, Baskoutas and Terzis, 2006].

The transition energies of quantum dots can be obtained analytically, numerically or from experiments. In this chapter, the transition energy, ΔE_g is explored for gold (Au), indium phosphide (InP), and cadmium selenide (CdSe) colloidal quantum

dots.

The energy of the exciton trapped in the spherical volume has been expressed by Brus [1983, 1984a,b], and Efros and Efros [1982] as

$$E_g = E_g^{bulk} + \Delta E_g = E_g^{bulk} + \frac{\hbar^2 \pi^2}{\mu 2R^2} - \frac{1.8e^2}{\epsilon R} \quad (5.1)$$

where E_g^{bulk} is the bulk band gap energy, ΔE_g the energy shift of the lowest excited state, $\hbar$ the Planck's constant divided by 2π , $\mu = (1/m_e^* + 1/m_h^*)^{-1}$ the reduced mass of the exciton, m_e^* the effective mass of electron, m_h^* the effective mass of hole, ϵ the dielectric constant, and R the radius. All the parameters are in their usual metric units. The first term on the right is the kinetic energy of the confined exciton and the second term represents the Coulomb interaction of the electron with the hole. This effective mass approximation (EMA) method assumes an infinite barrier at the interface with surrounding matrix material.

There are three other common energy-size relations that describe the transition energies and sizes:

1. The first is confinement energy, ΔE_g , with respect to N where N is the number of atoms. The relation between energy and N has been reported by Li et al. [2001a] and Zheng et al. [2004]),

$$E_g(N) \propto E_f N^{-\beta} \quad (5.2)$$

where E_f is the Fermi energy, N the number of atoms and β a constant. The values of β is $\frac{1}{3}$ for metals [Wood and Ashcroft, 1982, Zheng et al., 2004] and $\frac{2}{3}$ for semiconductors [Zheng et al., 2004].

2. The second is to the side-length/diameter, d , or radius, R ,

$$E_g(R) \propto R^{-\alpha} \quad (5.3a)$$

$$E_g(d) \propto d^{-\alpha} \quad (5.3b)$$

where d and R are the physical diameter and radius respectively, and α is a constant, which has a value of 2 for a quantum dot confined in an infinite well [Brus, 1984a]. The insulator material, gadolinium oxide, Gd_2O_3 has an energy gap shift towards the blue, similar to what is observed in semiconductor quantum dots, $\Delta E_g \propto 1/d^\alpha$, where $\alpha \approx 1.4$.

3. The third is to the volume, V_o [Li et al., 2001a],

$$E_g(V_o) \propto V_o^{-\gamma} \quad (5.4)$$

where V_o is the physical volume, and γ a constant. Li et al. [2001a] showed that the exponent γ depends on the dot's shape (e.g disk, ellipsoidal lens, cut-sphere lens and cone). For the CdS, from [Fonoberov and Pokatilov, 2002], $E_g^{sphere} = 4886.16/V_o^{2/3}$, $E_g^{tetra} = 6905.72/V_o^{2/3}$, and $E_g^{cube} = 4886.16/V_o^{2/3}$ where V_o has the unit of $\text{\AA}$.

In all three relations, the terms N , R , and V_o , are inversely proportional to the ground state transition energy, ΔE_g ($\Delta E_g = E_g - E_g^{bulk}$).

5.2 Electronic size and core-shell model

In this section, we develop the core-shell model based on size, N to obtain the electronic size of the quantum dots.

Equation (5.1) shows that electronic size, $R^{-\alpha}$, of the confined exciton in the quantum dot lies between $\alpha = 1$ (Coulomb term) and $\alpha = 2$ (kinetic term). For the sphere, the radius, R , is proportional to $V_o^{1/3}$, and R^2 is proportional to $V_o^{2/3}$. Therefore the size of the “exciton” size lies between $V_o^{1/3}$ and $V_o^{2/3}$, and is therefore smaller than the physical size, V_o . With this physical concept, we model the exciton volume as a core electronic sphere within the physical volume.

We consider two quantum dots (A and B) with transition energies, E_g^A and E_g^B , with electronic sizes of V_A and V_B respectively. The physical volume is $V_o = (a_o^3/N_{cell})N$, where a_o is the lattice constant and N_{cell} the number of atoms in each basic lattice cell. The ratio of their transition energies is

$$\frac{E_g^A}{E_g^B} = \frac{V_B}{V_A} \quad (5.5)$$

The core-shell model is represented in Figure 5.1 with the inner volume V_B and outer volume V_A , with $E_g^A < E_g^B$.

Figure 5.1: The core-shell model with “electronic” size of E_g^A and E_g^B are V_A and V_B respectively, and $E_g^A < E_g^B$.

The ratio of the inner electronic size, V_B , and the outer electronic size, V_A , is

$$V_B = \frac{4}{3}\pi \left(\frac{d}{2} - \frac{t}{2} \right)^3 = \frac{4}{24}\pi (d^3 - 3td^2 + 3t^2d - t^3) \quad (5.6a)$$

$$V_A = \frac{4}{3}\pi \left(\frac{d}{2} \right)^3 = \frac{4}{24}\pi d^3 \quad (5.6b)$$

$$\frac{V_B}{V_A} = 1 - \frac{3t}{d} + \frac{3t^2}{d^2} - \frac{t^3}{d^3} \quad (5.6c)$$

where d is the diameter and $t/2$ the thickness of the shell.

Using $d = ((a_o^3/N_{cell})N)^{1/3}$ [Fu and Zunger, 1997]), we can rewrite the ratio with respect to N and lattice constant, a_o , as

$$\frac{V_B}{V_A} = 1 - 3 \left(\frac{N_{cell}}{a_o^3} \right)^{1/3} t N^{-1/3} + 3 \left(\frac{N_{cell}}{a_o^3} \right)^{2/3} t^2 N^{-2/3} - \left(\frac{N_{cell}}{a_o^3} \right)^{3/3} t^3 N^{-1} \quad (5.7)$$

where the material dependency is imbedded within the lattice constant, a_o , and the size dependency within the number of atoms, N .

In the special case of $N=1$, where $\Delta E_g^B = E_g^{N=1} = E_f$, we obtain using

Equation (5.5) the following core-shell equation

$$\Delta E_g(N) = E_f \left(1 - 3 \left(\frac{N_{cell}}{a_o^3} \right)^{1/3} t N^{-1/3} + 3 \left(\frac{N_{cell}}{a_o^3} \right)^{2/3} t^2 N^{-2/3} - \left(\frac{N_{cell}}{a_o^3} \right)^{3/3} t^3 N^{-1} \right) \quad (5.8)$$

where E_f is the Fermi energy, $t/2$ the thickness of the shell, N_{cell} the number of atoms in the basic lattice cell, and a_o the lattice constant.

5.3 Results

The reported experimental or fitted data, in the form of $\Delta E_g(N)$, $\Delta E_g(R)$, or $\Delta E_g(V_o)$, are substituted into core-shell Equation (5.8) to obtain the values of t , $d - t$ and t/d for evaluation of the electronic size.

The results of the core-shell model for gold (Au), indium phosphate (InP) and cadmium selenide (CdSe) are given below.

5.3.1 Gold quantum dots

Gold (Au) nanoclusters have been extensively studied by Doremus [1964], Svergun et al. [1998], Wilcoxon et al. [1998], Zheng et al. [2004] and Gruber et al. [2008]. The gold material has a fcc-structure of 4 atoms per cell ($N_{cell} = 4$) with the lattice constant, $a_o = 4.078 \text{ \AA}$ [Kittel, 1996]. The metallic gold nanoclusters experience quantum confinement resulting in enhanced emission energies at small N .

The emission energy, E_g , of gold clusters decrease with increase in size, N , and varies with $N^{-1/3}$ [Zheng et al., 2004] for metallic quantum dots while for semiconductor quantum dots, it varies with $N^{-2/3}$. The experimental data of Zheng et al. [2004] are given in Table 5.1 and plotted in Figure 5.2, together with $N^{-1/3}$ and $N^{-2/3}$ as references. For metallic quantum dots such as gold, the E_{bulk} is zero and therefore $\Delta E_g = E_g$. The Fermi energy, E_f^{Au} , for gold at $N = 1$ is equal to 5.6 eV.

Table 5.1: Gold nanoclusters with values of ΔE_g with N . $\Delta E_g = E_g - E_{bulk}$ and E_{bulk} for metallic gold quantum dot is zero.

N	d (nm)	Emission, ΔE_g , (eV) [Zheng et al., 2004]
1	0.2568	5.6
5	0.4390	3.22
8	0.5135	2.72
13	0.6037	2.43
23	0.7302	1.65
31	0.8066	1.41

Figure 5.2: Correlation of the number of atoms, N , per cluster with emission energy, E_g , shown by the black circles and the fitted dotted line. The dashed line is $5.6/N^{1/3}$ and the dot-dashed line is $5.6/N^{2/3}$. The emission energy decreases with increasing number of atoms.

The fitted line equation for N between 1 and 31 is given by Equation (5.9a) below with $E_f = 5.6$ eV, and exponent $\beta = 0.3609$, which lies between $\frac{1}{3}$ and $\frac{2}{3}$. The goodness-of-fit chi-squared value is 0.1270 and the p-value of 0.0002924 is less than the 0.05 significance level, therefore we have a good fit. The core-shell equation is given in Equation (5.9b)

$$\Delta E_g = 5.6/N^{0.3609} \quad (5.9a)$$

$$\Delta E_g = 5.6 \left(1 - 3 \left(\frac{N_{cell}}{a_o^3} \right)^{1/3} t N^{-1/3} + 3 \left(\frac{N_{cell}}{a_o^3} \right)^{2/3} t^2 N^{-2/3} - \left(\frac{N_{cell}}{a_o^3} \right)^{3/3} t^3 N^{-1} \right) \quad (5.9b)$$

The ΔE_g — N experimental data is input into the core-shell Equation (5.9b) to solve for values of t , and given in Table 5.2. The Figure 5.3(a) and Figure 5.3(b) show the diameter, d , and t increases with N . The differences, $(d - t)$, also increases

with N as shown in Figure 5.3(c). The t increases with N , steeply at small N and continue to increase slowly at large N . The “electronic” size, $(d - t)$, continues to increase with large N .

The ratio of t/d is shown in Figure 5.3(d), and the t/d has a value of zero for $N = 1$, and about 0.85 in the bulk, $N = 8 \times 10^6$. At size $N = 1$, the “electronic” size is the same as the physical size. Though the “electronic” size and physical size increases with N , the relative size $(1 - t/d)$, decreases, e.g., they are 0.824 and 0.1474 for $N = 5$ and $N = 8 \times 10^6$ respectively.

Figure 5.3: Gold quantum dots: dashed line, d , dot-dashed line, $(d - t)$, and dotted line t (all in units of nm) against small N and large N , and t/d against large N .

Table 5.2: The ΔE_g is calculated using the fitted line equation. The values of t and t/d for gold quantum dots from N of 1 to 8192,000.

N	ΔE_g (eV)	t (nm)	d (nm)	$(d - t)$ (nm)	t/d
1	5.6	0	0.2568	0.2568	0
5	3.1326	0.0773	0.4392	0.3619	0.1760
8	2.6438	0.1137	0.5137	0.4000	0.2213
13	2.2188	0.1603	0.6040	0.4437	0.2653
23	1.8059	0.2295	0.7305	0.5010	0.3141
31	1.6214	0.2731	0.8070	0.5339	0.3384
64	1.2482	0.4045	1.0275	0.6230	0.3936
128	0.9719	0.5725	1.2946	0.7221	0.4422
256	0.7568	0.7941	1.6312	0.8371	0.4868
512	0.5893	1.0848	2.0551	0.9703	0.5278
1000	0.4628	1.4499	2.5689	1.1190	0.5644
2000	0.3603	1.9396	3.2367	1.2971	0.5992
4000	0.2806	2.5745	4.078	1.5035	0.6313
8000	0.2185	3.3952	5.1379	1.7427	0.6608
16000	0.1701	4.4534	6.4734	2.0200	0.6879
32000	0.1324	5.8146	8.156	2.3414	0.7129
64000	0.1031	7.5620	10.2759	2.7139	0.7358
128,000	0.0803	9.8011	12.9468	3.1457	0.7570
256,000	0.0625	12.6657	16.312	3.6463	0.7764
512,000	0.0487	16.3254	20.5518	4.2264	0.7943
1024,000	0.0379	20.9947	25.8937	4.8990	0.8108
2048,000	0.0295	26.9456	32.624	5.6784	0.8259
4096,000	0.0229	34.5217	41.1036	6.5819	0.8398
8192,000	0.0179	44.1581	51.7873	7.6292	0.8526

5.3.2 InP quantum dots

Indium phosphide (InP) is a binary semiconductor composed of indium and phosphorus and it has a face-centered cubic (“zincblende”) crystal structure, identical to most of the III-V semiconductors.

The term “effective size” has been popularly used to equate the experimentally measured side-length to an equivalent radius R , if the shape of the quantum dot is ellipsoidal or spheroidal. Fu and Zunger [1997] obtained for InP quantum dots, $E_g = 1.45 + 37.295/d^\alpha$, where $\alpha = 1.16$, and E_g has the unit of eV, while d has the unit of Å. They calculated the “effective” dot sizes using $d = (a_0/2)(N)^{1/3}$ where a_0 is the lattice constant and N the number of atoms in the dots. This gives “effective” sizes $d = 7.49, 8.95, 13.83, 18.57$, and 26.01 Å for quantum dots with 17, 29, 107, 259, and 712 atoms, respectively.

The fitted emission energies, E_g , of a reported experiment in Fu and Zunger [1997] is extracted and the ΔE_g are given in Table 5.3. The band gap shift, ΔE_g are obtained by subtracting the bulk band gap, $E_{bulk} = 1.45$ eV from the emission energy.

Table 5.3: InP nanoclusters with fitted ΔE_g with N .

N	d (nm)	ΔE_g (eV) [Fu and Zunger, 1997]
17	0.749	3.61
29	0.895	2.93
107	1.383	1.77
259	1.857	1.26
712	2.601	0.85

With the data in Table 5.3, we obtain the curve given by Equation (5.10) in terms of N and d respectively. The lattice constant, a_o , of InP is 0.58686 nm, with N_{cell} of 8 atoms in each unit cell.

Figure 5.4: InP, the plot of ΔE_g (eV) and N . The fitted line is $10.69903/N^{0.38666}$, the dashed line is $10.69903/N^{1/3}$ and the dot-dashed line is $10.69903/N^{2/3}$. The black dots are the fitted transition energies.

The fitted ΔE_f — N and ΔE_f — d are given by Equation (5.10a) and Equation (5.10b), respectively.

$$\Delta E_g = 10.69903/N^{0.38666} \quad (5.10a)$$

$$\Delta E_g = 2.58018/d^{1.16} \quad (5.10b)$$

The fitted Fermi energy, E_f , is 10.69903, a parameter in the core-shell equation.

$$\Delta E_g = 10.69903 \left(1 - 3 \left(\frac{N_{cell}}{a_o^3} \right)^{1/3} t N^{-1/3} + 3 \left(\frac{N_{cell}}{a_o^3} \right)^{2/3} t^2 N^{-2/3} - \left(\frac{N_{cell}}{a_o^3} \right)^{3/3} t^3 N^{-1} \right) \quad (5.11)$$

We use Equation (5.11) to calculate the values of t , and given in Table 5.4. Likewise the d , $(d - t)$, t curves are given at Figure 5.5(a) for small N and Figure 5.5(b) for large N , and the ratio t/d at Figure 5.5(d), respectively. An expanded view of the $(d - t)$ is shown in Figure 5.5(c).

Figure 5.5: InP quantum dots: dashed line, d , dot-dashed line, $(d - t)$, dotted line t , and t/d against N .

Table 5.4: The ΔE_g is calculated using the fitted line equation. The values of t , d , $(t - d)$ and t/d for InP quantum dots from N of 1 to 8192,000.

N	ΔE_g (eV)	t (nm)	d (nm)	$(d - t)$ (nm)	t/d
1	10.6990	0	0.2934	0.2934	0
17	3.5774	0.2308	0.7544	0.5236	0.3059
29	2.9099	0.3174	0.9015	0.5841	0.3521
107	1.7565	0.6303	1.3930	0.7627	0.4525
259	1.2479	0.9565	1.8704	0.9139	0.5114
712	0.8441	1.4964	2.6201	1.1237	0.5711
1000	0.7402	1.7297	2.9343	1.2046	0.5895
2000	0.5662	2.3090	3.6969	1.3879	0.6246
4000	0.4331	3.0586	4.6579	1.5993	0.6566
8000	0.3312	4.0258	5.8686	1.8430	0.6860
16000	0.2534	5.2707	7.3939	2.1232	0.7128
32000	0.1938	6.8692	9.3158	2.4466	0.7374
64000	0.1482	8.9182	11.7372	2.8190	0.7598
128,000	0.1134	11.5397	14.7879	3.2482	0.7803
256,000	0.0867	14.8889	18.6316	3.7427	0.7991
512,000	0.0663	19.1619	23.4744	4.3125	0.8163
1024,000	0.5074	24.6068	29.5759	4.9691	0.8320
2048,000	0.0388	31.5377	37.2633	5.7256	0.8463
4096,000	0.0297	40.3515	46.9488	6.5973	0.8595
8192,000	0.0227	51.5501	59.1518	7.6014	0.8715

An observation in Figure 5.5(a) is the crossover of t and $(d - t)$ at $N \approx 260$ where the “electronic” size is half the physical size. The $(d - t)$ value reaches about 8 nm at large N of 8×10^6 as given in Figure 5.5(c). The t/d value shown in Figure 5.5(d) has a value of 0.87 at $N = 8 \times 10^6$.

5.3.3 CdSe quantum dots

For CdSe quantum dots, an experimental data set from Murray et al. [1993] is given in Table 5.5.

Table 5.5: CdSe nanoclusters. ΔE_g and radius, R

R (nm)	ΔE_g (eV) [Murray et al., 1993]
0.615	1.27
1.045	0.87
1.155	0.77
1.725	0.53
1.845	0.51
2.185	0.42
2.445	0.37
2.57	0.31
4.155	0.17
5.785	0.14

The fitted equation is given by Equation (5.12) and shown in Figure 5.6. The goodness-of-fit chi-squared value is 0.01421 and the p-value of 1.0585×10^{10} is less than the 0.05 significance level, therefore we have a good fit. We calculated the Fermi energy to be 4.700744 based on $N = \frac{8}{a_0^3}(2R)^3$ where $N_{cell} = 8$.

$$\Delta E_g = 0.8436/R^{0.9094} \quad (5.12)$$

Figure 5.6: CdSe nanoclusters. The correlation of the ΔE_g with radius, R . The experimental data of Table 5.5 are shown by the black circles, with the curve-fitted dashed line. The transition energy decreases with increasing size of the nanoclusters.

The core-shell equation is given in Equation (5.13a) below and is used to calculate the values of t .

$$\Delta E_g = 4.700744 \left(1 - 3 \left(\frac{N_{cell}}{a_o^3} \right)^{1/3} t N^{-1/3} + 3 \left(\frac{N_{cell}}{a_o^3} \right)^{2/3} t^2 N^{-2/3} - \left(\frac{N_{cell}}{a_o^3} \right)^{3/3} t^3 N^{-1} \right). \quad (5.13a)$$

$$N = \frac{8}{a_o^3} (2R)^3 \quad (5.13b)$$

where the lattice constant $a_o = 0.6050$ nm.

The d , $(d - t)$, and t values are plotted and given in Figure 5.7(a) for small N and Figure 5.7(b) for large N . An expanded view of $(d - t)$ is given in Figure 5.7(c).

The “electronic” diameter $(d - t)$ value reaches about 12.2 nm at large N of 8×10^6 . The t/d in Figure 5.7(d) attains a value of 0.80 at $N = 8 \times 10^6$.

Figure 5.7: CdSe: dashed line, d , dot-dashed line, $(d - t)$, dotted line t , and t/d against N .

Table 5.6: The ΔE_g is calculated using the fitted line equation. The values of t , d , $(t - d)$ and t/d for CdSe quantum dots from N of 1 to 8192,000.

N	ΔE_g (eV)	t (nm)	d (nm)	$(d - t)$ (nm)	t/d
1	4.7007	0	0.3025	0.3025	0
67	1.3126	0.4260	1.2286	0.8026	0.3467
329	0.8105	0.9267	2.0882	1.1615	0.4437
445	0.7400	1.0627	2.3094	1.2467	0.4601
1483	0.5138	1.8004	3.4496	1.6492	0.5219
1815	0.4833	1.9613	3.6899	1.7286	0.5315
3014	0.4144	2.4250	4.3695	1.9445	0.5549
4224	0.3741	2.7865	4.8899	2.1034	0.5698
4905	0.3575	2.9621	5.1397	2.1776	0.5763
20731	0.2309	5.2662	8.3099	3.0437	0.6337
55953	0.1709	7.7367	11.5700	3.8333	0.6686
128,000	0.1330	10.5993	15.2450	4.6457	0.6952
256,000	0.1078	13.7502	19.2076	5.4574	0.7158
512,000	0.0873	17.7893	24.2000	6.4107	0.7350
1024,000	0.0708	22.9595	30.4901	7.5306	0.7530
2048,000	0.0573	29.5690	38.4151	8.8461	0.7697
4096,000	0.0465	38.0086	48.4000	10.3914	0.7853
8192,000	0.0377	48.7734	60.9802	12.2068	0.7998

5.4 Concluding remarks

In this chapter, the “core-shell” energy equation model of Equation (5.8) was developed, using the ratio of the volumes, which essentially breakdown the single term in the $\Delta E_g \propto N^{-\beta}$ relation into three terms: $N^{1/3}$, $N^{2/3}$ and $N^{3/3}$, and uses the fundamental parameters such as material-dependent lattice constant, a_o , and Fermi energy, E_f . By analogy, the $N^{1/3}$ term represents the length, $N^{2/3}$ the area, and $N^{3/3}$ the volume.

The “electronic” radii at large size, $(d - t)/2$, at $N \sim 8 \times 10^6$, are different from the exciton radius a_{ex} as summarized in Table 5.7, but they are about the same order of magnitude. For gold and InP, the “electronic” radii are smaller, while for the CdSe, it is slightly larger.

Table 5.7: The comparison of $(d - t)/2$ against the respective bulk effective Bohr radius, a_B^* , for gold, InP and CdSe quantum dots.

Material	$(d - t)/2$ (nm), $N \sim 8 \times 10^6$	a_B^* (nm)
Au	3.8	10
InP	3.8	20
CdSe	6.1	5

The “electronic” radius of our core-shell model has similar profile to the exciton radius, a_{ex} , i.e. it is small for small N , and increase in size with large N . The major shortcoming of this model is that the “electronic” radii do not attain an asymptotic limit at large N . This shortcoming shall be evaluated in our subsequent models.

In the next chapter, we shall explore another model based on $\Delta E_g = a + b/(V_o - V_t)$.

Chapter 6

Electronic Volume ($V_o - V_t$) Model

In this chapter, the electronic volume models are developed and evaluated for gold (Au), indium phosphate (InP) and cadmium selenide (CdSe) colloidal quantum dots.

We explore a new electronic volume model based on $\Delta E_g = a + b/(V_o - V_t)$ where we replace the usual V^γ with $(V_o - V_t)$. In this model, the V_t is negative at small size, ie., the $(V_o - V_t)$ is larger than the physical volume, V_o . This is phenomenally true of electron wave envelop functions that penetrate out of the quantum dot at strong confinement due to small size. The $(V_o - V_t)^{bulk}$ values approach an asymptotic limit at large size, however we need to assess whether the bulk “electronic” radii are close to the bulk effective Bohr radii for the respective gold, InP and CdSe quantum dots.

6.1 Introduction

In the previous chapter, we have established the core-shell model based on the number of atoms, N , and the lattice constant, a_o . Here we are going develop the electronic volume model based on V_o^γ . We have the basic electronic volume model and the $(V_o - V_t)$ electronic volume model.

6.2 Basic electronic model

The basic electronic volume of the quantum dot can be defined as V_o^γ of the basic equation $\Delta E_g = b/V_o^\gamma$, which can be translated to E_f/N^β given at Equation (6.1a). The electronic volume and electronic diameter, based on $b = E_f$, are given in Equation (6.1b) and Equation (6.1c) respectively, and shown pictorially in Figure 6.1.

$$\Delta E_g = b/V_o^\gamma \equiv E_f/N^\beta = E_f/\left(\frac{N_{\text{cell}}}{a_o^3}V_o\right)^\beta \quad (6.1a)$$

$$V_{\text{electronic}} = \left(\frac{N_{\text{cell}}}{a_o^3}V_o\right)^\beta \quad (6.1b)$$

$$d_{\text{electronic}} = (V_{\text{electronic}})^{1/3} \quad (6.1c)$$

where N is the number of atoms, E_f the Fermi energy at $N = 1$, N_{cell} the number of atoms in the basic lattice cell, a_o the lattice constant, and V_o the physical volume.

Physical Volume, $V_o = 4\pi R^3/3$

Figure 6.1: Basic electronic volume model, $V_{\text{electronic}}$

Based on work at the previous chapter, the $V_{\text{electronic}}$ for gold, InP and CdSe are realized as

$$V_{\text{electronic}}^{\text{Au}} = \left(\frac{4}{(0.4078)^3}V_o\right)^{0.36092} \quad (6.2a)$$

$$V_{\text{electronic}}^{\text{InP}} = \left(\frac{8}{(0.58686)^3}V_o\right)^{0.38666} \quad (6.2b)$$

$$V_{\text{electronic}}^{\text{CdSe}} = \left(\frac{8}{(0.6050)^3}V_o\right)^{0.30314} \quad (6.2c)$$

The plot of the electronic volume and electronic diameter with physical volume for gold, InP and CdSe quantum dots are given in Figure 6.2 and Figure 6.3 respectively. The $d_{electronic}$ continues to increase with V_o . This is contrary to the known confined exciton with bulk effective Bohr radius, a_B^* . The main limitation of this model is because the electronic volume continues to increase to infinity.

Figure 6.2: Gold (dashed line), InP (dotted line) and CdSe (dot-dashed line) nanoclusters, electronic volume, $V_{electronic}$.

Figure 6.3: Gold (dashed line), InP (dotted line) and CdSe (dot-dashed line) nanoclusters, electronic diameter, $d_{electronic}$

6.3 ($V_o - V_t$) electronic volume model

In this section, an alternative form of electronic volume based on the ($V_o - V_t$) volume model is developed. We evaluate the model with the colloidal spherical gold (Au), indium phosphate (InP) and cadmium selenide (CdSe) quantum dots. The physical representation of the volume model is given in Figure 6.4.

Physical Volume, $V_o = 4\pi R^3/3$

Figure 6.4: The energy-volume model depicted graphically.

Based on $\Delta E_g \propto V_o^{-\gamma}$, we generalized it to

$$\Delta E_g = a + b/V_o^\gamma \quad (6.3)$$

where if the value of γ is less than one, V_o^γ is smaller than V_o , and if γ is greater than one, V_o^γ is larger than V_o .

We define a new $(V_o - V_t)$ volume equation by replacing V_o^γ with $V_o - V_t$,

$$\Delta E_g = a + b/(V_o - V_t) \quad (6.4)$$

Equation (6.4) is well-behaved unless $V_o = V_t$ which will result in infinite energy. The exponent γ is now “embedded” into V_t .

We assume the constant a to be zero to satisfy the ΔE_g approximately zero in the bulk, and continue to adopt the constant b to be the Fermi energy, E_f . So we have,

$$\Delta E_g = \frac{E_f}{V_o - V_t} \quad (6.5)$$

Similarly, we used the available data from the literature, given in previous chapter, as input to calculate and evaluate V_t and $(V_o - V_t)$ for gold, InP and CdSe quantum dots.

6.4 Results

We used the same curve-fitted data from the previous chapter and they are normalized in terms of N , and then transform to $(V_o - V_t)$. The results of the $(V_o - V_t)$ model for gold (Au), indium phosphate (InP) and cadmium selenide (CdSe) quantum dots are given below.

6.4.1 Gold quantum dots

From $\Delta E_g^{(Au)} = 5.6/N^{0.3609}$ and $V_o = \frac{a_o^3}{4}N$, we obtain the $(V_o - V_t)$ volume equation for gold (Au) as,

$$\Delta E_g = 5.6 / \left(\frac{4}{a_o^3} V_o \right)^{0.3609} \equiv 5.6 / (V_o - V_t) \quad (6.6)$$

where the lattice constant $a_o = 0.4078$ nm and $N_{cell} = 4$.

The V_o and V_t values against N are plotted in Figure 6.5 for small $N < 30$ and Figure 6.6 for small $N < 1,000$. Of particular interest here are the negative values of V_t at small size of $N < 560$. This implies that $(V_o - V_t)$ has expanded over V_o . Such phenomena has been reported, [Kayanuma and Momiji, 1990], for electron and exciton confinement in very small quantum dots where the confinement is very strong. The negative values of V_t are small as shown in Table 6.1.

Figure 6.5: Gold quantum dots, the plot of V_o (dashed line) and V_t (continuous line) against N . The black dots are the fitted values of V_t .

Figure 6.6: Gold quantum dots, the crossover of V_t (continuous line) from negative to positive value. The black dots are the fitted values of V_t .

Table 6.1: Gold nanoclusters, the ΔE_g is calculated using the fitted line equation. The values of V_t , V_o and V_t/V_o for gold quantum dots from N of 1 to 8192,000.

N	ΔE_g (eV)	V_t (nm ³)	V_o (nm ³)	V_t/V_o
1	5.6	-0.9830	0.0169	0
5	3.1326	-1.7028	0.0847	-58.1656
8	2.6438	-1.9824	0.1356	-14.6194
13	2.2188	-2.3033	0.2204	-10.4505
23	1.8059	-2.7109	0.3899	-6.9528
31	1.6214	-2.9280	0.5255	-5.5718
64	1.2482	-3.4013	1.0850	-3.1348
128	0.9719	-3.5915	2.1701	-1.6549
256	0.7568	-3.0591	4.3403	-0.7048
512	0.5893	-0.8221	8.6806	-0.0947
1000	0.4628	4.8544	16.9544	0.2863
2000	0.3603	18.3693	33.9087	0.5417
4000	0.2806	47.8610	67.8175	0.7057
8000	0.2185	110.0058	135.635	0.8110
16000	0.1701	238.3556	271.27	0.8786
32000	0.1324	500.2696	542.54	0.9220
64000	0.1031	1030.7941	1085.08	0.9499
128,000	0.0803	2100.4431	2170.16	0.9678
256,000	0.0625	4250.7856	4340.32	0.9793
512,000	0.0487	8565.6545	8680.64	0.9867
1024,000	0.0379	17213.6081	17361.3	0.9914
2048,000	0.0295	34532.9090	34722.6	0.9945
4096,000	0.0229	69201.5540	69445.1	0.9965
8192,000	0.0179	138577.4272	138890.	0.9977

We have plotted the electronic diameter, $(V_o - V_t)^{1/3}$, in Figure 6.7. The core

diameter (side-length) attains a value of about 6.8 nm at $N = 8 \times 10^6$. This value differ from the bulk exciton radius, a_B^* of about 10 nm (or bulk exciton diameter of 20 nm).

Figure 6.7: Gold quantum dots, the plot of $(V_o - V_t)$ against N .

6.4.2 InP quantum dots

The $\Delta E_g^{(InP)}$ data for InP (see Table 5.3 given in previous chapter) is curve-fitted with Equation (6.7a) below in terms of diameter, d , and using $d = \left(\frac{a_o^3}{8}N\right)^{1/3}$, we obtain Equation (6.7b) in terms of N ,

$$\Delta E_g = 2.58018/d^{1.16} \quad (6.7a)$$

$$\Delta E_g = 10.69905/N^{0.38666} \quad (6.7b)$$

The equivalent $(V_o - V_t)$ volume equation, in terms of V_o is thus given by

$$\begin{aligned} \Delta E_g &= 10.69905/(V_o - V_t) \\ V_o &= \frac{a_o^3}{8}N \end{aligned} \quad (6.8)$$

where the $E_f = 10.69905$, lattice constant of InP is $a_o = 0.58686$ nm and $N_{cell} = 8$.

The results of the calculation for V_o and V_t are tabulated in Table 6.2 and plotted in Figure 6.8 for small $N < 712$. We have negative V_t for $N < 380$ indicating an expanded core larger than the physical volume, V_o .

Figure 6.8: InP quantum dots, the plot of V_o (dashed line) and V_t (continuous line) against small N . The black dots are the fitted values of V_t .

Table 6.2: The values of V_t , V_o and V_t/V_o for InP quantum dots from N of 1 to 8192,000.

N	ΔE_g (eV)	V_t (nm ³)	V_o (nm ³)	V_t/V_o
1	10.6990	-0.9747	0.0252	-38.6785
17	3.5774	-2.5612	0.4294	-5.9646
29	2.9099	-2.9440	0.7326	-4.0185
107	1.7565	-3.3877	2.7033	-1.2531
259	1.2479	-2.0296	6.5435	-0.3101
712	0.8440	5.3131	17.9884	0.2953
1000	0.7401	10.8102	25.2647	0.4278
2000	0.5661	31.6321	50.5293	0.6260
4000	0.4330	76.3529	101.059	0.7555
8000	0.3312	169.8178	202.117	0.8401
16000	0.2533	362.0073	404.235	0.8955
32000	0.1937	753.2626	808.469	0.9317
64000	0.1482	1544.7630	1616.94	0.9553
128,000	0.1133	3139.5171	3233.88	0.9708
256,000	0.0867	6344.3908	6467.75	0.9809
512,000	0.0663	12774.2269	12935.5	0.9875
1024,000	0.0507	25660.1623	25871.	0.9918
2048,000	0.0388	51466.3689	51742.	0.9946
4096,000	0.0296	103123.6717	103484.	0.9965
8192,000	0.0227	206496.9643	206968.	0.9977

The electronic diameter, $(V_o - V_t)^{1/3}$, are given in Figure 6.9, where the diameter is noted to be about 7.8 nm for $N = 8 \times 10^6$.

Figure 6.9: InP quantum dots, the plot of $(V_o - V_t)^{1/3}$ against N .

6.4.3 CdSe quantum dots

The ΔE_g^{CdSe} data, see Table 5.5 given in previous chapter, is given below in Equation (6.9a) in terms of radius, R , and using $2R = \left(\frac{a_o^3}{8}N\right)^{1/3}$, we obtain Equation (6.9b).

$$\Delta E_g = 0.84362/R^{0.90944} \quad (6.9a)$$

$$\Delta E_g = 4.70074/N^{0.30314} \quad (6.9b)$$

Using Equation (6.9b) and $V_o = \frac{a_o^3}{8}N$, the $(V_o - V_t)$ volume equation is thus

$$\Delta E_g = 4.70074 / \left(\frac{8}{a_o^3}V_o\right)^{0.30314} \equiv 4.70074 / (V_o - V_t) \quad (6.10)$$

where the lattice constant of CdSe is $a_o = 0.6050$ nm, $N_{cell} = 8$ and the curve-fitted $E_f^{N=1} = 4.70074$.

The results of the calculation for V_o and V_t are given in Table 6.3. From Figure 6.10, we note negative V_t values for $N < 160$, indicating an expanded core larger than the physical volume, V_o .

Figure 6.10: CdSe nanoclusters, the plot of V_o (dashed line) and V_t (continuous line) against N . The black dots are the fitted values of V_t .

Table 6.3: CdSe nanoclusters, the ΔE_g is calculated using the fitted line equation. The values of V_t , V_o and V_t/V_o for CdSe quantum dots from N of 1 to 8192,000.

N	ΔE_g (eV)	V_t (nm ³)	V_o (nm ³)	V_t/V_o
67	1.3126	-1.7202	1.8608	-0.9244
329	0.8105	3.3296	9.1293	0.3647
445	0.7400	5.9740	12.3263	0.4846
1483	0.5138	31.9148	41.0636	0.7772
1815	0.4833	40.5175	50.2434	0.8064
3014	0.4144	72.1104	83.4534	0.8640
4224	0.3741	104.3659	116.9301	0.8925
4905	0.3575	122.6496	135.7967	0.9031
20731	0.2309	553.5058	573.8561	0.9645
55953	0.1709	1521.3196	1548.8168	0.9822
128,000	0.1330	3507.7845	3543.12	0.9900
256,000	0.1078	7042.6434	7086.24	0.9938
512,000	0.0873	14118.6922	14172.5	0.9962
1024,000	0.0708	28278.6010	28345.	0.9976
2048,000	0.0573	56608.0564	56690.	0.9985
4096,000	0.0465	113278.8585	113380.	0.9991
8192,000	0.0377	226635.1347	226760.	0.9994

The electronic diameter, $(V_o - V_t)^{1/3}$, are given in Figure 6.11, and it is observed that the diameter is about 5 nm for $N = 8 \times 10^6$.

Figure 6.11: CdSe nanoclusters, the plot of $(V_o - V_t)^{1/3}$ against N .

6.5 Concluding remarks

The bulk electronic radius, $(V_o - V_t)^{1/3}/2$, for the three types of quantum dots lies between 2.5—3.8 nm. This is smaller than their respective bulk effective Bohr exciton radius, a_B^* of about 10 nm, 20 nm and 5 nm for gold, InP and CdSe, respectively, and they are tabulated in Table 6.4.

Table 6.4: The comparison of electronic radius, $(V_o - V_t)^{1/3}/2$, against the respective a_B^* for gold, InP and CdSe nanoclusters.

<i>Material</i>	$(V_o - V_t)^{1/3}/2$ (nm)	a_B^* (nm)
Au	3.4	10
InP	3.9	20
CdSe	2.5	5

The key strength of the $(V_o - V_t)$ electronic model is the electronic radii with the same order of magnitude as the effective Bohr exciton radii, a_B^* , for the gold, InP and CdSe quantum dots. The model highlights the expanded volume at small N where the electronic volume is larger than the physical volume.

Analytically, based on Equation (6.4), we need to include a non-zero constant, a to obtain

$$(V_o - V_t) = -\frac{b}{a}, \text{ for large } N \quad (6.11)$$

where we assume $\Delta E_g = 0$ for large N , and either a or b has negative value.

At this instance, we can have $(V_o - V_t)_{\text{large } N}$ equal to the effective Bohr exciton radius, a_B^* .

In the next chapter, we shall re-evaluate the assumption of $a = 0$ and $b = E_f$, and further refine the model.

Chapter 7

An Effective Volume Model for Spherical Quantum Dots

Nanoscale quantum dots experience quantum confinement resulting in enhanced emission energies. They have been used as bio-tags and currently applied to development of solar cells and quantum devices. The emission energies have been measured experimentally, and modeled analytically and numerically as “artificial atoms”. The onset of quantum size effect occurs around the characteristic length of 4–8 times the effective Bohr radius. The emission energies are dependent on size, shape and material. In this chapter, we investigate the dependency of confinement energies with the volume, and define the effective volume model and the analytical effective volume equations for the ground state exciton energies of the spherical quantum dots. The present model is validated using spherical quantum dots of the following materials, namely, cadmium sulphide (CdS), zinc oxide (ZnO), copper chloride (CuCl) and cadmium selenide (CdSe). It was found that the effective radius of the present model equates to the exciton radius, and we can calculate the exciton radii from the emission or ground state transition energies. The model can also be applied to quantum dots of other shapes, such as the pyramidal or dome shape.

7.1 Introduction

Interest in nanotechnology has increased exponentially since the 1980’s when size confinement effects were realized in semiconductor crystals, small metallic particles and aqueous colloids [Ekimov and Onushchenko, 1982, Efros and Efros, 1982, Rossetti and Brus, 1982, Wood and Ashcroft, 1982, Ekardt, 1985, Itoh and Furumiya, 1991, Laheld and Einevoll, 1997, Marin et al., 1998, Li et al., 2001a]. An exciton (electron-hole quasi-particle) is formed when an electron and a hole are bound together via Coulomb interaction. Due to screening of the Coulomb

interaction, the exciton radius is several times larger than the lattice spacing and are called the Wannier or Wannier-Mott exciton. The exciton behaves like an “artificial atom” with discrete energy levels. The exciton radius, a_{ex} , decreases from the bulk effective Bohr radius, a_B^* , with the reduction in size of the quantum dot due to quantum confinement. The transition energy of the exciton trapped in a spherical volume has been expressed by Brus [1983, 1984a,b], and Efros and Efros [1982],

$$\Delta E_g = \frac{2\hbar^2\pi^2}{\mu d^2} - \frac{3.6e^2}{\epsilon d} \quad (7.1)$$

where ΔE_g is the energy shift of the lowest excited state, $\hbar$ the Planck’s constant divided by 2π , $\mu = (1/m_e^* + 1/m_h^*)^{-1}$ the reduced mass of the exciton, m_e^* the effective mass of electron, m_h^* the effective mass of hole, ϵ the dielectric constant, and d the quantum dot diameter. All the parameters are in their usual metric units. The first term on the right is the kinetic energy of the confined exciton and the second term represents the Coulomb interaction of the electron with the hole. This effective mass approximation (EMA) method assumes an infinite barrier at the interface with surrounding matrix material. Equation (7.1) was refined by Kayanuma [1986, 1988] with separate equations for strong confinement,

$$\Delta E_g = \frac{\hbar^2}{2\mu} \left(\frac{\pi}{R} \right)^2 - 1.786 \frac{e^2}{\epsilon R} - 0.248 E_{R_y^*} \quad (7.2)$$

and for weak confinement

$$\Delta E_g = -E_{R_y^*} + \frac{\hbar^2}{2M} \left(\frac{\pi}{R} \right)^2 \quad (7.3)$$

where the Rydberg’s energy $E_{R_y^*} = \mu e^4 / 2\epsilon^2 \hbar^2$, $M = m_e^* + m_h^*$ is the translational mass, and R the radius. The strong confinement occurs at length scale lesser than two times the effective Bohr radius, and weak confinement greater than four times, and in between two to four times we have the intermediate confinement regime.

The confinement energies of quantum dots are size-, shape- and material-dependent [Baskoutas and Terzis, 2006, 2008]. The energy shift or transition energy, ΔE_g , is inversely proportional to size represented by its length, d , radius, R or volume V_o . For example, the energy shift in Equation (7.2) is dependent on radius, R , and the square of the radius, R^2 . Fu and Zunger [1997] obtained $\Delta E_g = 37.295/d^n$ where $n = 1.16$ for indium phosphate (InP), and Wang and Zunger [1994a] obtained $\Delta E_g = 88.34/d^n$ where $n = 1.37$ for silicon (Si). Using numerical simulations, Fonoberov and Pokatilov [2002] obtained the energies for different CdS quantum dot shapes, such that $E_g^{\text{tetrahedra}} = 6905.72/V_o^{2/3}$, $E_g^{\text{cube}} = 5641.09/V_o^{2/3}$ and $E_g^{\text{sphere}} = 4886.16/V_o^{2/3}$, with the length unit in Å. Li et al. [2001a] fitted the

transition energies with volume, $\Delta E_g \approx V_o^{-\gamma}$, to obtain the value of γ of 0.38 for disk shape, 0.35 for ellipsoidal lens shape, 0.31 for cut spherical lens shape, and 0.27 for cone shape. Ngo et al. [2006] introduced the effective volume by replacing V_o with V_{eff} , such that $\Delta E_g \approx 1/V_{\text{eff}}^{2/3}$ for quantum dots in infinite barrier.

In this work, we seek to develop an effective size model. We define the effective volume model and the effective volume equations for the confinement energies in spherical quantum dots. The effective volume, V_{eff} , is calculated from ΔE_g which can be obtained analytically, numerically or from experiments. The chapter is organized as follows: after the description of the effective volume model, we present the results of our comparison of the R_{eff} and exciton radii for CdS, ZnO, CuCl and CdSe quantum dots. Finally the conclusions are drawn and summarized.

7.2 Effective volume model

The usual energy-size relations are based on d^α [Wang and Zunger, 1994a, Fu and Zunger, 1997], V_o^γ [Li et al., 2001a, Fonoberov and Pokatilov, 2002], and N^β [Zheng et al., 2004], where the exponents α , β and γ are constants. We aim to develop a “universal” effective size model that is independent of the exponent. The volume is chosen so that it can be applied to quantum dots of all shapes.

The basis of our effective volume model is the $\Delta E_g \propto V_o^\gamma$ relation. We define a new effective volume model,

$$\Delta E_g = a + b/V_{\text{eff}} \quad (7.4a)$$

$$R_{\text{eff}} = \left(\frac{V_{\text{eff}}}{4\pi/3} \right)^{1/3} \quad (7.4b)$$

where V_{eff} is the effective volume, R_{eff} the effective radius, while a and b are parameter constants.

We can determine the constant a using the boundary condition that the confinement energy, ΔE_g , equals $-E_{R_y^*}$, at the bulk when $V_o \rightarrow \infty$, as indicated by the weak confinement Equation (7.3). For the constant, b , we approximate it from the gradient of the differential of the dominant kinetic term with respect to R , of the strong confinement Equation (7.2). The effective volume equation is realized as

$$\Delta E_g = -E_{R_y^*} + \frac{\hbar^2 \pi^2}{\mu} / V_{\text{eff}} \quad (7.5a)$$

$$a = -E_{R_y^*} \quad (7.5b)$$

$$b = \hbar^2 \pi^2 / \mu \quad (7.5c)$$

The effective volume, V_{eff} , is calculated from Equation (7.5a) by fitting the ΔE_g — V_o data from experiments, numerical simulations or analytical equations. As a good data set is required to validate our model, we apply the finite element based numerical simulations to obtain a complete range of sizes and materials for quantum dots of spherical shape. The ΔE_g is obtained from the summation of the electron ground state energy, E_e , and the hole ground state energy, E_h .

We also employ the finite barrier model as the infinite barrier EMA model with $1/R^2$ scaling of the kinetic term has been shown to be inaccurate by over-estimating the band gaps for sizes where the confinement are significant [Sapra et al., 2003, Kayanuma and Momiji, 1990]. The finite barrier has been shown to be accurate and widely adopted with the single-particle finite well effective mass approximation model [Pellegrini et al., 2005, Zhang and Sharma, 2005, Ngo et al., 2006]. Thus the finite depth/width square well EMA (FWEMA) method [Pellegrini et al., 2005, Baskoutas and Terzis, 2008, Marin et al., 1998] and the numerical finite element approach are used here to solve the Schrödinger equation,

$$-\frac{\hbar^2}{2m_e^*} \nabla_e^2 \psi(r) - \frac{\hbar^2}{2m_h^*} \nabla_h^2 \psi(r) + V_e(r_e) \psi(r) + V_h(r_h) \psi(r) = E \psi(r) \quad (7.6a)$$

$$V_e = \begin{cases} 0, & 0 \leq r_e \leq R \\ V_e, & R \leq r_e \leq \infty \end{cases} \quad (7.6b)$$

$$V_h = \begin{cases} 0, & 0 \leq r_h \leq R \\ V_h, & R \leq r_h \leq \infty \end{cases} \quad (7.6c)$$

where r_e and r_h are respectively the electron and hole position relative to the center of the sphere, V_e and V_h are the barrier height of the confining potential for the electron and hole respectively, and R the radius of the sphere.

We assume the materials are isotropic with similar potential barrier for electron and holes, i.e., $V_e = V_h$. The electron and hole energies are simulated separately [Laheld and Einevoll, 1997] using the finite element method.

Alternatively we can adopt an analytical approach where $\Delta E_g = B_X$, with the exciton binding energy as defined by Takagahara [1993],

$$B_X \approx \frac{\pi^2 E_{R_y^*}}{(R/a_B^*)^2} \quad (7.7a)$$

$$a_B^* = \hbar^2 \epsilon / \mu e^2 \quad (7.7b)$$

where B_X has the unit of eV, and the effective Bohr radius a_B^* the unit of m.

7.3 Results

We selected the spherical colloidal quantum dots of four material types, namely: cadmium sulphide (CdS) and cadmium selenide (CdSe) which are III–V compound semiconductors with respective direct band gaps of 2.5 eV and 1.7–1.8 eV; zinc oxide (ZnO) [Cheng et al., 2006, Klingshirn, 2007] which is a II–VI compound wide-gap semiconductor with a direct band gap of 3.4 eV; and copper chloride (CuCl) [Ferhat et al., 2001] which is a colorless I–VII compound semiconductor with large band gap of 3.4 eV. In semiconductors, the electrons can be excited from the valence band to the conduction band. The electron and the remaining hole in the valence band experience attractive Coulomb interaction such that they can form bound electron-hole pair, the exciton.

The simulation parameters for CdS, ZnO, CuCl and CdSe colloidal quantum dots are given at Table 7.1.

Table 7.1: The simulation parameters for CdS, ZnO, CuCl and CdSe colloidal quantum dots. $V_{e(h)}^{matrix}$ is the confinement potential of electron (hole) in the matrix/barrier. The values of some reported effective Bohr exciton radius, a_B^* , are also provided.

	CdS ¹	ZnO ²	CuCl ³	CdSe ⁴
$m_e^* (m_o)$	0.18	0.24	0.44	0.13
$m_h^* (m_o)$	0.53	2.27	3.6	0.4
$V_{e,h}^{matrix} \text{ (eV)}$	2.25	1.5	1.5	1.3
$a_B^* \text{ (nm)}^{11}$	2.06 ⁵	0.9 ²	0.68 ⁶	5–6 ⁷
	2.8 ⁴	1.25 ⁵	0.99 ⁸	
	3.0 ⁹	2.34 ¹⁰		

¹Lippens and Lannos [1989], Einevoll [1992]

²Fonoberov and Balandin [2004]

³Ferhat et al. [2001]

⁴Lippens and Lannos [1989]

⁵Baskoutas and Terzis [2008]

⁶Itoh and Furumiya [1991]

⁷Lippens and Lannos [1989], Laheld and Einevoll [1997], Senger and Bajaj [2003]

⁸Senger and Bajaj [2003]

⁹Krishna and Friesner [1991], Marin et al. [1998]

¹⁰Senger and Bajaj [2003], Hsu et al. [2007]

¹¹Reported or calculated with the reported m_e^* , m_h^* and ϵ_r parameter values.

The FWEMA numerical results for $\Delta E_g = E_e + E_h$ are shown in Figure 7.1, together with the experimental and numerical data from earlier reports [Li and Wang, 2005, Lin et al., 2005, Itoh and Kirihara, 1984, Sapra and Sarma, 2004, Murray et al., 1993, Rossetti et al., 1984, Wang and Herron, 1990, Krishna and Friesner, 1991, Bawendi et al., 1989]. The confinement energies of the FWEMA simulation, shown with the dashed lines, are more accurate than the infinite well EMA, as shown in the representative Figure 7.1(a) for CdS, Figure 7.1(b) for ZnO, Figure 7.1(c) for CuCl and Figure 7.1(d) for CdSe. The present simulations are in good agreement with the experimental data, for example from Rossetti et al. [1984] and Wang and Herron [1990] for CdS quantum dots, Li and Wang [2005] and Lin et al. [2005] for ZnO quantum dots, Itoh and Kirihara [1984] for CuCl quantum dots, and Murray et al. [1993] and Bawendi et al. [1989] for CdSe quantum dots.

 (a) CdS, ΔE_g

 (b) ZnO, ΔE_g

 (c) CuCl, ΔE_g

 (d) CdSe, ΔE_g
Figure 7.1: The plots of ΔE_g against R for CdS, ZnO, CuCl and CdSe colloidal quantum dots.

7.3.1 Effective volume, V_{eff}

The simulated ΔE_g data set are substituted into Equation (7.5a) to calculate V_{eff} and R_{eff} . The values of the material-dependent parameters a and b are given in Table 7.2 for reference. The plot of V_{eff} against R , where $R = (V_o/(4\pi/3))^{1/3}$, for CdS, is shown in Figure 7.2. We also show the V_{eff} calculated using the analytical data set of Kayanuma (Equation (7.2)) and Takagahara (Equation (7.7a)). The V_{eff} results from Kayanuma's strong confinement equation, which is based on the infinite potential barrier model and shown with dotted lines, are found to be significantly higher. The FWEMA results, indicated by circle, are congruent to those using the binding energy, shown with the dot-dashed lines.

Figure 7.2: The plot of V_{eff} against R for CdS quantum dots.

In Figure 7.3, we show the entire set of results by plotting V_{eff} for ZnO, CuCl and CdSe colloidal quantum dots. The present FWEMA-derived V_{eff} are coincident with those using Takagahara's analytical approach [Takagahara, 1993]. It is also observe that V_{eff} increases asymptotically as R increases.

Figure 7.3: The plot of V_{eff} against R for ZnO, CuCl and CdSe quantum dots.

7.3.2 Bulk effective radius, R_{eff}^{∞}

We shall now evaluate the effective radius in the bulk. At large R , we can apply Equation (7.5a) with $(E_e + E_h) = 0$. Following simplification, we obtain $V_{eff}^{\infty} = \frac{\hbar^2 \pi^2 / \mu}{2\epsilon^2 \hbar^2 / \mu \epsilon^4}$ which reduces to $2\pi^2 (a_B^*)^2$. The bulk effective radius, R_{eff}^{∞} , can then be written as

$$R_{eff}^{\infty} = (3\pi/2)^{1/3} (a_B^*)^{2/3} \quad (7.8)$$

where R_{eff}^{∞} is effectively a $\frac{2}{3}$ power factor of the effective Bohr exciton radius a_B^* .

The R_{eff}^{∞} is plotted against the effective Bohr radius, a_B^* , in Figure 7.4, and the $R_{\text{eff}}^{\infty} = a_B^*$ line is given as a reference. The figure shows R_{eff}^{∞} is higher than a_B^* when a_B^* is smaller than ≈ 5 nm. The presently calculated R_{eff}^{∞} from Equation (7.8) for the CdS, ZnO, CuCl and CdSe quantum dots give respective values of 2.8nm, 1.5nm, 1.3nm and 4.9nm, which are higher than the effective Bohr radius, see Table 7.2.

The differences increases for quantum materials with larger effective Bohr radius, for example gold with $a_B^* \approx 10$ nm. The difference is likely due to the approximation of the value of b , which was derived from the kinetic term, while neglecting the Coulomb and other minor terms.

Figure 7.4: The plot of bulk effective radius, R_{eff}^{∞} , against the effective Bohr radius, a_B^* . The $R_{\text{eff}}^{\infty} = a_B^*$ dot-dashed line is given as a reference.

Table 7.2: The a and b of $\Delta E_g = a + b/V_{\text{eff}}$, a_B^* and R_{eff}^{∞} for CdS, ZnO, CuCl and CdSe colloidal quantum dots. The a_B^* values are calculated with the selected m_e^* , m_h^* and ϵ_r . The b_1 and the respective R_{eff}^{∞} are also provided.

	CdS	ZnO	CuCl	CdSe
ϵ_r	5.5	3.7	5.0	9.3
$a = -E_{R_y^*}$ (eV)	-0.0604	-0.2157	-0.2134	-0.01543
$b = \hbar^2 \pi^2 / \mu$	5.5971	3.4649	1.9181	7.66524
R_{eff}^{∞} (nm)	2.8	1.5	1.3	4.9
a_B^* (nm)	2.17	0.90	0.67	5.016
$b_1 = \frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{3\mu^2e^2}$	2.5727	0.6633	0.2747	8.1591
R_{eff}^{∞} (nm) (using b_1)	2.17	0.90	0.67	5.016

7.3.3 Effective radius, R_{eff} , and exciton radius, a_{ex}

Here we use $\Delta E_g = B_X$ from Equation (7.7a). The plot of R_{eff}/a_B^* against R , using B_X , is given in Figure 7.5. The figure shows that the effective radius should

attain a bulk limit of the effective Bohr radius.

Figure 7.5: The plot of ratio of effective radius and effective Bohr radius, R_{eff}/a_B^* , against the radius, R , using the binding energy, B_X ($\Delta E_g = B_X$). The continuous, dot-dashed, dashed and dotted lines respectively denote the CuCl, ZnO, CdS and CdSe quantum dots respectively.

With the bulk effective radius equal to effective Bohr radius, $R_{\text{eff}}^\infty = a_B^*$, we can calculate a new b . Following algebraic manipulation, we obtain the new expression of b , which we shall denote as b_1 , where $b_1 = 2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)/(3\mu^2e^2)$ and their values for the various quantum dots are given in Table 7.2. The new effective volume equation with b_1 is realized as,

$$\Delta E_g = -E_{R_y^*} + \frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{(3\mu^2e^2)V_{\text{eff}}} \quad (7.9)$$

By substituting $\Delta E_g = B_X = \frac{\pi^2 E_{R_y^*}}{(R/a_B^*)^2}$ in Equation (7.9), we obtain

$$\frac{\pi^2 E_{R_y^*}}{(R/a_B^*)^2} = -E_{R_y^*} + \frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{(3\mu^2e^2)V_{\text{eff}}} \quad (7.10)$$

and following simplification, we obtain

$$V_{\text{eff}} = \frac{4\pi R^2(a_B^*)^3}{3(R^2 + \pi^2(a_B^*)^2)} \quad (7.11a)$$

$$R_{\text{eff}} = \left(\left(\frac{4\pi R^2(a_B^*)^3}{3(R^2 + \pi^2(a_B^*)^2)} \right) \frac{4\pi}{3} \right)^{1/3} \quad (7.11b)$$

$$\frac{R_{\text{eff}}}{a_B^*} = \left(\frac{(R/a_B^*)^2}{(R/a_B^*)^2 + \pi^2} \right)^{1/3} \quad (7.11c)$$

Since a_B^* is fixed for a material, R_{eff}/a_B^* in Equation (7.11c) is only dependent on

R . The R_{eff}/a_B^* normalized profile is given in Figure 7.6, and it is consistent with the a_{ex} probability wave-function of $\langle \Psi | 1/r | \Psi \rangle$ from Senger and Bajaj [2003]. In the strong confinement region, where R/a_B^* is less than 2, the exciton radius (represented by R_{eff}) is less than $0.7 a_B^*$, and in the intermediate confinement region, where R/a_B^* lies between 2 and 4, the exciton radius lies between 0.7 – $0.85 a_B^*$. At the weak confinement limit, where $R/a_B^* \approx 8$, the exciton radius is at $0.97 a_B^*$, which is near the bulk confinement. This validates the onset of quantum confinement occurs around the characteristic length between 4–8 times the effective Bohr radius.

Figure 7.6: The plot of the ratio of effective radius and effective Bohr radius, R_{eff}/a_B^* , against the ratio of radius and effective Bohr radius, R/a_B^* , using the Equation (7.11c). This normalized line is common to all QD materials. The R_{eff}/a_B^* attain the asymptotic limit of one at large R/a_B^* .

The effective volume model enables the calculation of the exciton volume by substituting the transition energy into the effective volume equation.

7.4 Concluding remarks

We have evaluated the exciton energies of CdS, ZnO, CuCl and CdSe spherical quantum dots. The exciton energy and exciton volume of the quantum dots are dependent on sizes and materials. In this work, we have developed and defined the effective volume model, and derived the effective volume equations which were applied with simulated FWEMA energy data and the analytical binding energy. The results from the present model demonstrated that the effective radius, R_{eff} , is qualitatively and quantitatively consistent to the exciton radius, a_{ex} . We have thus concluded the equivalence between the effective radius, R_{eff} , and the exciton radius, a_{ex} .

We have derived an analytical effective volume equation that enable the exciton

radius to be calculated from experimentally measured or numerical values of the exciton energy.

The present model, which is based on volume, can be easily extended to other quantum dot shapes such as pyramidal or dome shapes. The detailed exploration of the effective volume model to other shapes will be addressed in the next chapter.

Chapter 8

General Effective Volume Model of InAs/GaAs SAQDs

The self-assembled quantum dots are currently intensively studied for applications in solar cells, quantum lasers and qubits devices. The characterization of the structural and electronic properties continues to be important to the selection of the optimal compound materials, shapes and sizes of the quantum dots. We define a new general effective volume model and derived the effective volume equation applicable to all materials, shapes and sizes. The equation relates the ground state transition energies and the effective volume of the quantum dot. We simulate the confinement effects of realistic and “fictitious” shapes, such as pyramid, truncated pyramid, “bead” and “hourglass”, of the indium arsenide quantum dots to calculate the effective volume/radius. It was observed that the ground states carriers have a propensity to remain spherical and occupy the broad space in the quantum dot, and the confinement strength is determined by the smallest/narrowest spatial dimension of the quantum dot. It was also determined that our effective radius is similar to the exciton radius.

8.1 Introduction

The ground state exciton energy is basically the summation of the electron and hole kinetic energies, the coulomb potential between the electron and hole, and the spatial correlation between the electron and hole. The analytical equation was developed by Brus [1984b] and enhanced by Kayanuma [1988],

$$E_g(R) = E_g(\infty) + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786}{\epsilon_r R} - 0.248 E_{R_y}^* \quad (8.1)$$

where $E_g(R)$ is the ground state energy, $E_g(\infty)$ the bulk band gap energy, $\hbar$ the

Planck's constant, $\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ the reduced mass of an electron-hole (e-h) pair, and m_e^* and m_h^* the effective masses of electron and hole, respectively. The Rydberg energy is $E_{R_y} = \mu e^4 / 2\epsilon_r^2 \hbar^2$, and ϵ_r is the effective dielectric constant. The first term is the kinetic energy of the confined exciton and the second term represents the Coulomb interaction of the electron with the hole. The $1/R^2$ kinetic term is dominant at small R while the $1/R$ Coulomb term becomes significant as R increases. The last correlation term is a small material-dependent constant. The effect of incomplete confinement of electrons and holes is quite large in the strong confinement regime while $R < a_B^*$ where $a_B^* = \hbar^2 \epsilon / \mu e^2$ is the effective Bohr radius [Elliott, 1957]. Based on experimental results the infinite barrier model (Equation (8.1)) with $1/R^2$ scaling of the kinetic term has been shown to be inaccurate by over-estimating the band gaps for sizes where the confinement are significant. Substantial efforts have also been given to experiments and numerical simulation to obtain the exciton energies.

Wang and Zunger [1994a] reported that the energy band gap variation with cluster size was almost identical for spheres, rectangular boxes, and cubes, and Albe et al. [1998] observed that the energetic range of the spectra of the CdSe clusters with oblate and prolate elliptic configurations and spherical form were identical. Li et al. [2001a] reported a 0.1 eV difference in electron ground state energy for InAs/GaAs dots of the same volume but different shapes.

Using numerical simulations, Li et al. [2001a] showed that the electron energies were dependent on dot volume V^γ , where γ is a constant, and $V^{2/3}$, in infinite barrier. The dependence of transition energies, fitted to $E \propto V^{-\gamma}$ to obtain the γ parameter, are 0.38 for disk shape, 0.35 for ellipsoidal lens shape, 0.31 for cut spherical lens shape and 0.27 for cone shape. Pryor [1999] indicated that the island volume matters more than shape. Ngo et al. [2006] reported that the effective volume of the pyramidal shape is smaller than that of the cuboid shape with the same physical volume, and those with narrow tips (e.g., pyramidal shape) have a higher energy state compared to those with broad tips. This was attributed to smaller effective volume in quantum dots with narrow tips.

The relations between size and shapes shall be evaluated with the present generalized effective volume model. In this chapter, we will first define the generalized effective volume model applicable to quantum dots of all sizes, shapes and material-types. Next we provide the results of our numerical simulation of the transition energies, ΔE_g , for the usual sphere, pyramid, semi-sphere shapes, and the fictitious “bead” and “hourglass” shapes. We then evaluate the effective volume/radius using the simulated data before concluding our findings.

8.2 Models and Methods

8.2.1 Effective volume model

In this section, the effective volume model of the exciton (bound electron and hole quasi-particle) confined in the quantum dot is derived based on the known empirical energy-volume relation, $\Delta E_g \propto V_o^{-\gamma}$, where V_o is the physical volume and γ is a constant. Mathematically it is possible to fix the value of γ and adopt an effective volume model similar to that of Ngo et al. [2006], where $V_o^{-\gamma}$ is replaced with $V_{\text{eff}}^{-2/3}$, and $V_{\text{eff}} = V_o$ if $\gamma = 2/3$.

The transition energy ΔE_g correlates to the exciton binding energy. In the energy-volume relation, the V_o^γ could be a measure of the electronic volume of the exciton as shown in Figure 8.1. The values of V_o^γ at size of 100nm radius are 5nm, 12nm and 30nm for γ values of 1/3, 1/2 and 2/3 respectively. The limitation of this model is that the electronic volume continues to increase indefinitely, contrary to the exciton volume which should eventually attain the bulk effective Bohr radius. Similarly, Ngo et al. [2006] effective volume, where $V_{\text{eff}}^{2/3} = V_o^\gamma$, also suffers from the same limitation.

Figure 8.1: The electronic volume and electronic radius based on γ values of 1/3 (dashed line), 1/2 (dot-dashed line) and 2/3 (dotted line).

Thus, a volume model that gives a finite bulk exciton radius is required. We define a new general effective volume model that should be applicable to all shapes,

$$\Delta E_g = a + b_1/V_{\text{eff}} \quad (8.2a)$$

$$R_{\text{eff}} = \left(\frac{V_{\text{eff}}}{4\pi/3} \right)^{1/3} \quad (8.2b)$$

where ΔE_g is the ground state transition energy, with the bulk value of $\Delta E_g^{\text{bulk}} = 0$, a and b_1 are constants, V_{eff} the effective volume, and R_{eff} the effective radius of an equivalent sphere.

The bulk effective volume, $V_{\text{eff}}^{\text{bulk}}$, when ΔE_g approaches zero, is equal to a constant $-\frac{b_1}{a}$ and is therefore bounded, provided $a \neq 0$.

The values for constants a and b_1 can be obtained from two bulk boundary conditions. At the bulk, the exciton energy is $-E_{R_y^*}$, and the effective exciton Bohr radius is a_B^* . Therefore the constant, a is equal to $-E_{R_y^*}$, and b_1 is calculated to be $\frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{(3\mu^2e^2)}$. We realize the effective volume equation as,

$$\Delta E_g = -E_{R_y^*} + \frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{(3\mu^2e^2)V_{\text{eff}}} \quad (8.3)$$

Equation (8.3) needs to be evaluated thoroughly, for a complete data set of selected shapes, and sizes ranging from 100's of atoms to 1,000,000 atoms and more. This will be carried out by numerical simulation here.

8.2.2 Self-assembled InAs/GaAs quantum dots

The InAs/GaAs self-assembled quantum dots (SAQDs) have been well studied through experiments [Wang et al., 2000a, Kim et al., 1998, Anders et al., 2002, Ling et al., 2008] and numerical simulations [Cusack et al., 1996, Costales and Pandey, 2002, Schliwa et al., 2007]. We shall employ the finite barrier confinement potential model as it has been shown to be accurate, and has been widely adopted for the single-particle finite well effective mass approximation (FWEMA) [Pellegrini et al., 2005, Zhang and Sharma, 2005, Ngo et al., 2006] method.

The SAQDs come in a few regular shapes such as tetrahedral/pyramid, truncated pyramid, dome, lens, semi-sphere and semi-spheroidal. The actual shapes are more complex with different facets in different orientations and experiments have shown that the growth of the quantum dots start with the pyramidal shape and enlarge to the lens- or dome-shape. There are instances where both shapes co-exist together. The shape is flattened when the capping layer is added. As experimental data are not available for all sizes and shapes, the transition energies for a wide range of sizes and shapes are generated numerically using the FWEMA method. The InAs/GaAs quantum dot system is chosen as it is one of the most well-researched self-assembled quantum dot, where more experimental data are available for comparison.

We evaluate the InAs/GaAs SAQD nanostructures of various shapes indicated in Table 8.1. The regular quantum dot shapes are the pyramid, the sphere, and dome (simulated as semi-sphere). We have chosen other shapes such as the cube, cylinder, “bead”, “hourglass” and hexahedral, so as to provide a better understanding of the confinements in shapes with round and sharp tips. The geometry of the pyramidal, “bead” and “hourglass” shaped quantum dots are shown in Figure 8.7. We simulate the pyramidal quantum dots of fixed aspect ratio, h/b , in Figure 8.2(b), fixed height, h , in Figure 8.2(c), fixed base-length, b , in Figure 8.2(d). The “bead” and “hourglass” shapes, as shown in Figures 8.2(e), 8.2(f), are chosen to evaluate the effect of the narrow constriction on the envelop functions and the transition energies. The Schrödinger equation and the material parameters are given in Equation (8.4).

Figure 8.2: Pyramidal-, bead- and hourglass-shaped quantum dots. The bead- and hourglass-shape are formed by two truncated cones.

The quantum dots are simulated using the finite element method (FEM) which solves the Schrödinger equation variationally for the ground states of the electron and hole,

Table 8.1: Shapes of quantum dots analyzed in this study.

Shape of QDs	Descriptions
b1	fixed base = 12.4 nm
b2	fixed base = 24 nm
b3	fixed base = 36 nm
b4	fixed base = 18 nm
h	fixed height = 3 nm
h2	fixed height = 2 nm
r1	fixed aspect ratio, $h/b = 1:3$
r2	fixed aspect ratio, $h/b = 1:4$
r3	fixed aspect ratio, $h/b = 1:2$
r4	fixed aspect ratio, $h/b = 1:1$
sphere (sph)	fixed aspect ratio
cube (cube)	fixed aspect ratio
cylinder (cyl)	fixed aspect ratio, $h/d = 1:4$
hemisphere (semisph)	fixed aspect ratio
hexahedral (rect)	fixed aspect ratio, $h/b = 1:2$
bead (bead)	fixed aspect ratio, $h/d = 1:1$
hourglass (hglass)	fixed aspect ratio, $h/d = 1:1$

$$\begin{aligned}
 & -\frac{\hbar^2}{2m_e^*} \nabla_e^2 \psi(r) - \frac{\hbar^2}{2m_h^*} \nabla_h^2 \psi(r) + V_e(r_e) + V_h(r_h) = E\psi(r) \\
 & \left\{ \begin{array}{l} m_e^* = \begin{cases} 0.024 m_e & \text{QD} \\ 0.067 m_e & \text{Matrix} \end{cases} \\ V_q = 0 \text{ eV} \\ V_m = 0.77 \text{ eV} \\ m_h^* = \begin{cases} 0.4 m_e & \text{QD} \\ 0.5 m_e & \text{Matrix} \end{cases} \\ V_q = 0 \text{ eV} \\ V_m = 0.33 \text{ eV} \end{array} \right. \quad (8.4)
 \end{aligned}$$

where m_e is the mass of the electron, m_e^* and m_h^* the effective masses of electron and hole respectively, and $V_{q(m)}$ the potential offset in the quantum dot (matrix). The quantum dot refers to the InAs, and the matrix is the GaAs substrate. The strained-induced band gap is equal to 0.52eV (1.52eV - 0.77eV - 0.33eV). We define the ground state confinement transition energy as $\Delta E_g = E_e + E_h$, where E_e and E_h are the ground state energies of the electron and hole respectively.

8.3 Results

The present numerical results are compared with available experimental data [Kim et al., 1998, Anders et al., 2002, Offermans et al., 2005, Wang et al., 2000a, Ling et al., 2008, Song et al., 2004] in Figure 8.3. The sphere shape has the lowest energy for the same volume and it is the “least confined shape”. It is observed that for large sizes of more than 5000 nm³, the shape effect on transition energy is small except for the fixed height quantum dots of 2nm and 3nm. This is akin to the 3D quantum dot being transform into a 2D quantum well.

Figure 8.3: InAs/GaAs QD with finite barrier, ΔE_g (eV) versus V_o (nm³). Comparison of the present numerical data with experiments. [Experiment Sources: exptAnders [Anders et al., 2002], exptKim [Kim et al., 1998], exptOffermans [Offermans et al., 2005], exptSong [Song et al., 2004], exptWang [Wang et al., 2000a], exptLing [Ling et al., 2008]]

The shapes of SAQDs obtained from experiments are generally pyramidal or semi-sphere. They do not follow a fixed height to base length (h/b) ratio as they grow in size. The pyramidal shapes are favored at small size and they are transformed to lens/dome shape as the size increases. The final shapes also depend on whether they are capped or not. When the quantum dot is first capped, the top is flattened while the base is elongated and the resultant shape remains with further capping. In Figure 8.4, we can see that the quantum dots from Kim et al. [1998] are pyramidal and the ΔE_g decreases linearly with height, h . At h of about 6 nm, the pyramidal shape transforms into dome shape. Both pyramidal and dome shapes co-exist between height values of 6 nm to 7.5 nm. There is also a linear trend in the decrease of ΔE_g with base-length, b . The present numerical results are in good agreement with experiments.

Figure 8.4: InAs/GaAs QD with finite barrier, ΔE_g (eV) versus b (nm) and inset (ΔE_g (eV) versus h (nm)). [Experiment Sources: exptAnders [Anders et al., 2002], exptKim [Kim et al., 1998], exptOffermans [Offermans et al., 2005], exptSong [Song et al., 2004], exptWang [Wang et al., 2000a], exptLing [Ling et al., 2008]]

The transition energies and their spatial dimensions such as length, area, volume and area/volume ratio are analyzed. The transition energies, ΔE_g , are dependent on shape and size, where the size is denoted by the physical volume, V_o , physical area, A_o and physical lengths such as base length, b , height, h , radius, R , or diameter, d .

Figure 8.5 shows the variation of the ΔE_g with volume, V_o , and R_o (in the inset), for pyramidal quantum dots of different aspect ratios, fixed heights and fixed base lengths. As expected, the ΔE_g reduces with increase in volume and (equivalent) radius. The shape effect on ΔE_g is discernable below radius values of about 12–13 nm. The fixed height quantum dots of $h=2$ nm and $h=3$ nm have a non-zero ΔE_g due to strong confinement in the height-axis. As the height of 3 nm is much smaller than the effective Bohr radius, $h \ll a_B^*$, where $a_B^* = \frac{\hbar^2 \epsilon_r \epsilon_o (4\pi)}{\mu e^2}$, the quantum dot does not attain the bulk status as the size increase in the other two spatial dimensions. It becomes a quantum well with a 2D exciton. It is observed that the energy-volume profiles of the pyramidal quantum dots with fixed aspect ratios are close to each other, and different from those quantum dots with fixed base-length.

Figure 8.5: Pyramidal InAs/GaAs QDs with finite barrier, ΔE_g (eV) versus V_o (nm^3) with inset for ΔE_g (eV) versus R_o (nm), where R_o is the equivalent radius of the volume, V_o .

Next, we evaluate the variation of ΔE_g with the surface area, A_o , and the surface/volume ratio, A_o/V_o , in Figure 8.6. The ΔE_g increases rapidly at small A_o for fixed base-length quantum dots, and at small height values. A small decrease in h and thus a small increase in A_o/V_o , causes a large increase in the carrier confinement. The A_o/V_o ratio of the quantum dots decreases with increasing size as expected, due to area being a squared term while the volume is a cubic term.

Figure 8.6: Pyramidal InAs/GaAs QD with finite barrier, ΔE_g (eV) versus A_o (nm^2).

The plots of ΔE_g against h and b are given in Figure 8.7(a) and Figure 8.7(b) respectively. We observe wide dispersions of ΔE_g with height and base-length, and particularly so for quantum dots with either fixed height or fixed base length in the range of 2nm to 12nm.

Figure 8.7: Pyramidal InAs/GaAs QD with finite barrier, ΔE_g (eV) versus h (nm) and b (nm)

8.3.1 Effective radius, effective exciton Bohr radius and effective exciton radius

The energy envelop functions of the electron and hole in the pyramidal quantum dots with fixed height of 3nm, semi-sphere and sphere quantum dots with radius of 3nm, are given in Figure 8.8 and, for illustration, the pyramidal quantum dots with base-length 12.4nm and height 48nm in Figure 8.9. The electron and hole envelop functions are generally confined within the quantum dot except when at small size where, in particular, the electron envelop function penetrates out of the quantum dot. For larger sizes, the envelop function is smaller than the physical volume.

Figure 8.8: The density envelop functions of electrons and holes in pyramidal quantum dots with fixed height $h=3\text{nm}$, base-lengths of $b=36\text{nm}$, 18nm and 4.5nm , and semi-sphere and sphere of 3nm radius.

Figure 8.9: The density envelop functions of pyramidal InAs/GaAs quantum dots with finite barrier, $b=12.4\text{nm}$, $h=48\text{nm}$ (electron and hole).

Based on the InAs/GaAs material parameters given in Equation (8.4), $\epsilon_r=12.3$, and $E_{R_y^*} = \frac{\mu e^4}{2(4\pi\epsilon_r\epsilon_o)^2\hbar^2}$, we arrive at the constant values of $a=-0.002036$ eV and $b_1=202.632$ nm³.eV, and $\Delta E_g = -0.002036 + 202.632/V_{\text{eff}}$. We calculate the bulk effective radius, $R_{\text{eff}}^{\text{bulk}}$, equal to $(\frac{202.632}{E_{R_y^*}}/\frac{4\pi}{3})^{1/3} = 28.7$ nm. All the quantum dots, which are unrestrained in any spatial dimensions, should attain the asymptotic limit for R_{eff}^∞ , equal to the effective Bohr radius, a_B^* .

The R_{eff} for various representative shapes (pyramids, semi-sphere, bead and hourglass) are given in Figure 8.10. The profiles are obtained by curve-fitting of the numerical data and extrapolating to $R=1000\text{nm}$. As the size of the quantum dot increases, the R_{eff} increases. For the unconstrained quantum dots, the R_{eff} should attain the asymptotic limit of the effective Bohr radius, a_B^* , of 28.7nm. For the quantum dots that are constrained in one or more spatial dimensions, the R_{eff} attain an asymptotic limit less than the effective Bohr radius. The asymptotic limit of R_{eff} for the fixed height, $h=3\text{nm}$, is about 7–8 nm at radius $R=1000\text{nm}$. The quantum dots with fixed base-length of 12.4nm is semi-constrained. It is assessed that profiles of our R_{eff} is similar to a_{ex} .

Figure 8.10: InAs/GaAs QD with finite barrier, R_{eff} versus R_o for various QD shapes for R_o up to 1000nm. [semi-sphere (blue), pyramid type-r1 (orange), bead (red), hourglass (black), pyramid type-b1 (magenta), and pyramid type-h (green)]

8.3.2 Bead and hourglass shapes

Here, we take a closer look at two quantum dot shapes formed by two truncated cones. The bead and hourglass shapes are formed by two truncated cones with the bead created by joining the bigger frustums and the hourglass by joining the smaller frustums. Both shapes have different geometry with similar volume for the same radii and height. The representative envelop functions are shown in Figure 8.11 and Figure 8.12 for large size of $R=12\text{nm}$ and $h=24\text{nm}$, and small size of $R=2\text{nm}$ and $h=4\text{nm}$. The envelop functions in the bead shape look very similar to the semi-sphere and sphere. The hourglass shape has a constriction that elongates the envelop functions.

Figure 8.11: Bead-shape InAs/GaAs QD with finite barrier, $d=4\text{nm}$ and $h=4\text{nm}$, $d=24\text{nm}$ and $h=24\text{nm}$: density envelop functions for electron and hole.

Figure 8.12: Hourglass-shape InAs/GaAs QD with finite barrier, $d=4\text{nm}$ and $h=4\text{nm}$, $d=24\text{nm}$ and $h=24\text{nm}$: density envelop functions for electron and hole.

The hourglass shape has a higher confinement effect because of the narrow constriction at the center, and this is exemplified in the effective radii given in Figure 8.10. Both shapes attain the bulk effective exciton Bohr radius at large R .

8.4 Concluding remarks

We have defined a general effective volume model and derived the effective volume equation, where we can calculate V_{eff} and the (equivalent) radius, R_{eff} . We have carried out numerical simulation to obtain a good set of data for various sizes and shapes of quantum dots to evaluate our model. The results show that the ground state wave functions are confined in the broad volume in the quantum dots, avoiding the shape tips. The spherical shape is the least confining as every space is occupied

or occupiable. For the quantum dots with restraint in any spatial dimension, e.g., fixed height or fixed base-length, they do not attain the bulk properties due to strong confinement in that spatial dimension. We calculated the effective radius, R_{eff} , and determined that it is akin to the exciton radius, a_{ex} . The effective radius is equal to the effective Bohr radius in the bulk. In summary we have verified that the exciton radius is shape- and size-dependent and we have defined a general effective volume model with the effective radius, R_{eff} that measures the exciton volume, and this is applicable to all sizes and shapes, and materials.

Chapter 9

Conclusions and Future Work

We have developed several models of quantum dots which have assisted in the understanding of the confinement energies with respect to their sizes, shapes and materials.

Our first model, the core-shell model, included the $N^{1/3}$ (representing length), $N^{2/3}$ (representing area), $N^{3/3}$ or N (representing volume) terms in a polynomial equation, where N is the number of atoms. The “electronic” size, $(d - t)$ increases monotonically with the size of quantum dot, and the “electronic” radius at $N = 8 \times 10^6$ are within the same order of magnitude with the bulk exciton radius, a_B^* .

Our second model, the basic electronic model, and the third model, the electronic volume model, $(V_o - V_t)$, are alternative approaches. The electronic radius, likewise do not approach a limit size for large N , and is of the same order of magnitude to the Bohr exciton radius, a_B^* , at $N = 8 \times 10^6$. All the three models have the profile of the electronic size similar to the exciton size, a_{ex} , in quantum dots. We then needed a model with the electronic radius approaching the Bohr radius, a_B^* in the bulk.

In our fourth model, the effective volume model, we included mathematically the bulk binding energy, $E_{R_y^*}$, and replaced the numerator E_f with a calculated $2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)/(3\mu^2e^2)$. The effective volume model has been developed with a strong mathematical foundation where $\Delta E_g = a + b_1/V_{\text{eff}}$ where $b_1 = 2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)/(3\mu^2e^2)$.

The effective volume model is applicable to sizes of the quantum dots from the very small sizes of quantum dots to the bulk. We have shown the model to be applicable to quantum dots of all practical shapes and materials.

We then developed the effective volume equation that can be simply used to determine the exciton size with measured or calculated emission energy using

$$a_{\text{ex}} = R_{\text{eff}} = \left(\frac{2\pi\hbar^4(4\pi\epsilon_r\epsilon_o)}{(3\mu^2e^2)} / \frac{4\pi}{3}(\Delta E_g + E_{R_y^*}) \right)^{1/3} \quad (9.1)$$

and the effective volume can be rewritten as

$$\Delta E_g = -E_{R_y^*} + \frac{4}{3\pi} \left[\frac{\hbar^2 \epsilon}{\mu e^2} \right] \left(\frac{\hbar^2 \pi^2}{2\mu} \frac{1}{\frac{4\pi}{3} a_{\text{ex}}^3} \right) = -E_{R_y^*} + \frac{1}{\pi^2} [a_B^*] \left(\frac{\hbar^2 \pi^2}{2\mu} \frac{1}{a_{\text{ex}}^3} \right) \quad (9.2)$$

where we can see that the ΔE_g is dependent on the ratio, a_B^*/a_{ex}^3 .

9.1 Achievements

The key contribution of the work is the definition of a new effective volume model that depicts the exciton volume, and we have attained several achievements in the computational modeling and analysis of the quantum dots. In summary, we have:

1. Modeled a new interfacial capping layer (ICL) to study its effect on strains in the pyramidal InAs/GaAs QDs. We determined that the inclusion of the ICL layer, with higher elastic constant than the InAs and GaAs, produces more accurate strained band gap energy in the pyramidal InAs/GaAs self-assembled quantum dot.
2. Developed a core-shell electronic size model that enable the analysis of the quantum dots based on lattice constant, a_o , length $N^{1/3}$, area $N^{2/3}$ and volume $N^{3/3}$. The bulk electronic radius obtained are of the same order of magnitude as the bulk effective Bohr radius, a_B^* .
3. Developed an electronic volume ($V_o - V_t$) model that embed the exponent γ . This is a shape-invariant model. Similarly, the bulk electronic radius obtained are of the same order of magnitude as the bulk effective Bohr radius, a_B^* .
4. Developed the effective volume model, $\Delta E_g = a + b_1/V_{\text{eff}}$, that depicts the exciton volume. We defined the value of b_1 that give the bulk effective volume equal to the bulk exciton volume. The R_{eff} is equal to the bulk effective Bohr radius, a_B^* .
5. Generalized the effective volume model for all practical shapes of quantum dots. We show the effective volume and bulk effective radius can be used to explain the confinement of exciton in overly constrained quantum dots such as quantum well where the width is smaller than the Bohr exciton radius, and the differences in confinement energies for different shapes.

9.2 Future works

The definition of the effective volume model is just the beginning of more interesting work which can be done. We have applied it to quantum dots of various shapes and materials. It has to be “fortified” with applications to further validate the model, and the model could be further refined. For future works, we propose a few interesting problems,

1. Evaluation of shape transformation of the cylinder quantum dot to disk-shaped QD ($h \ll R$) [Sugawara, 1995], cylindrical rod-shaped quantum dot ($h > R$) [Steiner et al., 2004, Planelles et al., 2009] and quantum wire ($h \gg R$) [Voss et al., 2009].
2. The application of the effective volume model for biexcitons in quantum dots [Scholes, 2008, Sewall et al., 2009, Mlinar and Zunger, 2009, Bansal et al., 2009].
3. The effective volume model could be enhanced for quantum dot molecules [Ortner et al., 2005].
4. The application of the effective volume model for graphene quantum dots in Husler and Egger [2009].
5. An interesting extension is the evaluation of how the effective volume model interprets the expanded electronic volume at very small sizes.

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