2004 Debye Lecture 3
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Semiconductor Nanocrystals
Quantum Dots Part 1
Basic Physics of Semiconductor Quantum Dots
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Bulk Semiconductor
- Conduction Band
- Valence Band
- Energy Gap

Quantum Dot
- Like a Molecule
- Highest Occupied Molecular Orbital
- Lowest Unoccupied Molecular Orbital
Quantum Confinement
Low Dimensional Structures

$\rho_c(E) \propto \sqrt{(E - E_c)}$

$\rho_c(E) = \text{const} \tan t$

$\rho_c(E) \propto \frac{1}{\sqrt{(E - E_n)}}$

$\rho_c(E) \propto \delta(E - E_n)$
Particle-in-a-Sphere

\[ \Phi(r, \theta, \phi) = C \frac{j_l(k_{n,l}r)Y_l^m(\theta, \phi)}{r} \]

\( Y_l^m(\theta, \phi) \) is a spherical harmonic

\( j_l(k_{n,l}r) \) is the l\textsuperscript{th} order spherical Bessel function

\[ k_{n,l} = \frac{\alpha_{n,l}}{a} \]

Discrete energy levels

\[ E_{n,l} = \frac{\eta^2 k_{n,l}^2}{2m_o} = \frac{\eta^2 \alpha_{n,l}^2}{2m_o a^2} \]

solutions give hydrogen-like orbitals with quantum numbers

\( n \) (1, 2, 3 …)

\( l \) (s, p, d …)

\( m \)

size-dependence
The Quantum Dot is a Semiconductor

The Effective Mass Approximation
parabolic conduction and valence bands

Direct Bandgap Semiconductor

Bloch’s Theorem

\[ \Psi_{nk}(\vec{r}) = u_{nk}(\vec{r}) \exp(ik \cdot \vec{r}) \]

with periodicity of crystal lattice

Free particles treated by effective mass:

- describing graphically the curvature of the bands
- representing the potential presented by the lattice
Combining the Effective Mass Approximation with a Spherical Boundary Condition

**Single Particle (sp) Wavefunction**

1. \[ \Psi_{sp}(\mathbf{P}) = \sum_{k} C_{nk} u_{nk}(\mathbf{P}) \exp(i\mathbf{k} \cdot \mathbf{P}) \]
   
   linear combination of Bloch functions

2. \[ \Psi_{sp}(\mathbf{P}) = u_{n0}(\mathbf{P}) \sum_{k} C_{nk} \exp(i\mathbf{k} \cdot \mathbf{P}) = u_{n0}(\mathbf{P}) f_{sp}(\mathbf{P}) \]
   
   assume \( u_{nk} \) has weak \( k \)-dependence

Envelope Function Approximation valid for \( r_{QD} > \) lattice constant which for QDs is given by the "Particle-in-a-Sphere"

3. \[ u_{n0}(\mathbf{P}) = \sum_{i} C_{ni} \varphi_{n}(\mathbf{P} - \mathbf{P}_{i}) \]
   
   linear combination of atomic orbitals with atomic wavefunctions \( \varphi_{n} \) (n= CB or VB) \( i=\)lattice sites
Coulomb Attraction

Bulk semiconductors, Coulomb attraction creates bound excitons

Confinement Energy $\propto 1/a^2$
Coulomb Attraction $\propto 1/a$

For small a:
- Confinement Energy $>$ Coulomb Attraction
  - Electron and hole are treated independently
- Coulomb interaction added as a correction

\[
E_{ehp}(n_hL_hn_eL_e) = E_g + \frac{n^2}{2a^2} \left\{ \frac{\varphi_{n_hL_h}^2}{m_{\text{eff}}^v} + \frac{\varphi_{n_eL_e}^2}{m_{\text{eff}}^c} \right\} - E_{\text{coulomb}}
\]

For $1S_e$ pairs of states $E_{\text{coulomb}} = 1.8e^2/\epsilon a$

Size Dependence of Electronic Structure

Decreasing Dot Diameter
Development of Electronic Structure
Similar to Length Dependence in 1D polyenes

- p-orbitals form \( \pi \)-bonds with associated energy levels with an energy separation in the visible

- Example of alternating double/single bond
  \( \pi \)-bond extends over many C atoms

- Polyene's with increasing chain length

- Ground

- HOMO (Highest Occupied Molecular Orbital)

- LUMO (Lowest Unoccupied Molecular Orbital)
Size Dependent Absorption
Example: CdSe

Absorbance (arbitrary units)
Semiconductor Materials

Range from 30 nm QDs to bulk crystal

Graph from H. Weller, Pure Appl. Chem. 72, 295 (2000)
Absorption Spectra of Semiconductor Nanocrystals

Changing the Core

InAs

HgS

InP

PbSe

PbS

PbTe

A. P. Alivisatos, UC Berkeley

O. Micic, A. Nozik, NREL

C. B. Murray, IBM
Real Band Structure

Example: CdSe

Cd 5s orbitals
2-fold degenerate at k=0

Se 4p orbitals
6-fold degenerate at k=0
Introduces splitting of bands

E

E_g

\Delta_{cf}

k

\Delta_{so}

hh

heavy hole

lh

light hole

so

spin-orbit splitoff

J = L + S
where
L=orbital angular momentum
S=spin angular momentum

J good quantum number due to strong spin-orbit coupling

J=1/2
J=3/2
Size Evolution of Electronic States

\[ F = J + L \]
where \( L \) = envelope angular momentum
\( J \) = Bloch-band edge angular momentum

Hole states labeled by \( n_h L_F \) [\( L_F = L + (L+2) \)]
Electron states labeled \( n_e L_e \)


Low Band gap InAs modeling must also account for valence-conduction band coupling.

InAs

CdSe

\[ 1S_{3/2} \rightarrow 1S_e \]
\[ 2S_{3/2} \rightarrow 1S_e \]
\[ 1P_{3/2} \rightarrow 1P_e \]
Selection Rules

\[ P = |\langle \Psi_e | \hat{p} \cdot \hat{\rho} | \Psi_h \rangle|^2 \]

- polarization vector of light
- momentum operator
- acts only on unit cell portion of wavefunction

\[ P = |\langle u_c | \hat{p} \cdot \hat{\rho} | u_v \rangle|^2 |\langle f_e | f_h \rangle|^2 \]

\[ P = |\langle u_c | \hat{p} \cdot \hat{\rho} | u_v \rangle|^2 \delta_{n_e,n_h} \delta_{L_e,L_h} \]

Overlap of the electron and hole wavefunctions within the QDs
Towards the Homogeneous Distribution: Photoluminescence and Photoluminescence Excitation

Photoluminescence Excitation
“smallest” QDS

Photoluminescence Excitation
“largest” QDS

Distribution in ensemble from size, structure, and environmental inhomogeneities
Fluorescence Line Narrowing and Photoluminescence Excitation

Band Edge Exciton Structure

Splitting due to crystal field, non-spherical shape, and exchange interactions of quantum dots

Single Molecule Spectroscopy

Diffraction Limited Spot
Fluorescence Intermittancy in CdSe QDs

On-period decreases with increasing illumination intensity

Off-period intensity independent

Excitation every $10^{-5}$ sec
Relaxation every $10^{-8}$ sec

But occasionally
Two electron-hole pairs may exist in a single QD

Auger ionization
Probability of photoionization/excitation $10^{-6}$
Neutralization time $\sim 0.5$ sec

Auger Ionization

Photoluminescence

Auger quenching

Ionized nanocystal

Auger autoionization

Thermal autoionization

Consistent with single molecule spectroscopy and photodarkening observed in QD doped glasses

Single Dot Spectroscopy

Individual quantum dots

Histogram of 513 43 Å QDs Including all phonon lines

Single Quantum Dot Emission

Spectral diffusion driven by environment

Metal Nanoparticles

Surface Plasmon Resonance

- dipolar, collective excitation between negatively charge free electrons and positively charged core
- energy depends on free electron density and dielectric surroundings
- resonance sharpens with increasing particle size as scattering distance to surface increases
Electronic Properties of Semiconductor and Metal Nanoparticles

Charge not completely solvated as in infinite solid

Nanoparticle capacitance

\[ C = 4\pi \varepsilon_0 \varepsilon a \]

Charging Energy

\[ E_c = \frac{e^2}{2C(a)} \]

Coulomb blockade at \( k_B T < E_c \)


Structure from discrete electronic states of metal NC
STM Measurements on Single QDs

InAs QDs

Synthesis of monodisperse CdSe nanocrystals

\[
\text{Cd}(\text{CH}_3)_2 + (\text{oct})_3 \text{PSe} \xrightarrow{HDA-\text{TOPO}-\text{TOP}, 300^\circ C} \text{CdSe} + \ldots
\]

TEM and HRTEM images of as-prepared CdSe nanocrystals.

UV-Vis and PL spectra of CdSe nanocrystals in growth at 300°C

Wet Chemical Synthesis of PbSe Nanocrystals and Superlattices

Synthesis

\[ \text{Pb(OAc)}_2 + \text{R}_3\text{PSe} \]

oleic acid,
\[ \text{R}_3\text{P}, \text{T}=150 \text{ C} \]

\[ \text{R= octyl} \]

PbSe

Size Selective Processing

Size selective precipitation in solvent/ non solvent pairs like hexane-methanol

Self Assembly

Evaporation of the solvent
PbSe Nanocrystals and Nanowires

**Nanocrystals:**

1.5 – 10 nm diameters
100 – 100 000 atoms

PbSe Nanocrystal

Small Bandgap (0.28 eV, cf CdSe : 1.70 eV) ⇒ IR detector, IR diode Laser Material
Larger Bohr Radius (PbSe 46 nm, CdSe 12nm) ⇒ Strong Confinement of Electron-Hole Pair
Larger Optical Nonlinearity, Thermoelectric Cooling (ZT = 1 : PbTe)
Semiconducting, Solar Cells, Thermoelectric, Biological Application

PbSe Nanowire

Solution Phase Synthesis using the Nanoparticles as a Building Block
Formation of the Nanowires from the Self Assembling the Particles
Controlling the wire Properties by Changing the Size and Shape of the Particles
Semiconducting device, Interconnect, Building Blocks for the Nanodevice
Monodisperse Colloid Growth (La Mer)

Concentration of Precursors (arbitrary units)

Injection

Growth

From Solution

Ostwald Ripening

Staturation

Nucleation Threshold

0 200 400 600 800 1000

Seconds

Monodisperse Colloid Growth (La Mer)
Size selective processing:

![Diagram of Size Selective Processing](image)

**Growth Solution**

- 37 Å Major Dia. 
  - σ = 12%

**Size Selected**

- 39 Å Major Dia. 
  - σ = 4.5%

**Diagram Details**

- Center to Center Distance $R$
- Normalized Counts
- Energy (arbitrary units)
- Steric Repulsion ($R^{-12}$)
- van der Waals ($R^{-6}$)
- Attraction

**Additional Details**

- MeOH
- Hexane BuOH
Results of size selected precipitation

(a) 37Å+12%
(b) 39Å+8%
(c) 40Å+5%
(d) 42Å+<4%
(e) 39Å+11%
(f) 41Å+6%
(g) 45Å+<4%
Absorption and Photoluminescence of PbSe Nanocrystals

PbSe Nanocrystals

PbSe nanowires
Based on IR & TEM
Calculated using Scherrer Formula (XRD)
PbSe in Phosphate Glass
Effective Mass Approx.
Shape Change from Sphere to Cubic and SAXS in Polymer Matrix

Experiment Sphere Particle
D = 9.8 nm, Rg = 3.8 nm
(σ = 8 %)

Experiment Cubic Particle
L = 10.5 nm, Rg = 5.25 nm
(σ = 10 %)

K.-S. Cho, W. Gaschler
PbSe Quantum Cubes
WAXS of 10 nm PbSe quantum cubes slowly deposited from toluene (top) and rapidly precipitated from methanol (bottom)
Shape evolution of PbSe Nanocrystals

Highly symmetric rock salt structure
Modeling of x-ray diffraction:

The Debye equation which is valid in the kinematical approximation is shown in equation 4.6\(^{(8)}\).

\[
I(q) = I_o \sum_m \sum_n F_m F_n \frac{\sin(qr_{m,n})}{qr_{m,n}}
\]

(4.6)

Where \(I(q)\) is the scattered intensity, \(I_o\) is the incident intensity, \(q\) is the scattering parameter \([q = 4\pi \sin(\theta)/\lambda]\) for X-rays of wavelength \(\lambda\) diffracted through angle \(\theta\). The distance between atoms \(m\) and \(n\) is \(r_{mn}\). A discrete form of the Debye is shown in equation (4.7)\(^{(9)}\).

\[
I(q) = I_o \frac{f^2(q)}{q} \sum_k \frac{\rho(r_k)}{r_k} \sin(qr)
\]

(4.7)

where \(I_o\) is the incident intensity, \(f(q)\) is the angle dependent scattering factor \(q\) is the scattering parameter \([q = 4\pi \sin(\theta)/\lambda]\) for X-rays of wavelength \(\lambda\) diffracted through angle \(\theta\). The sum is over all inter atomic distances, and \(\rho(r_k)\) is the number of times a given interatomic distance \(r_k\) occurs. Since the number of discrete interatomic distances in an ordered structure grows much more slowly than the total number of distances, using the discrete form of the equation is significantly more efficient in the simulation of large crystallites\(^{(9)}\).
Modeling Stacking faults

Modeling NP Shape

Scattered Intensity (arbitrary units)

Equivalent Diameter ~63Å

Spherical 1:1

Prolate 1.22
Small angle X-ray Scattering SAXS

\[ I(q) = I_o N[(\rho - \rho_o)^2 F(q)^2 \frac{4}{3} \pi R^3 \left[ 3 \sin(qR) - qR \cos(qR) \right]] \]

Where \( \rho \) and \( \rho_o \) are the electron density of the particle and the dispersing medium respectively. \( I_o \) is the incident intensity and \( N \) is the number of particles. \( F(q) \) is the material form factor (the fourier transform of the shape of the scattering object) and is the origin of the oscillations observed. Thus for a spherical particle of radius \( R \)

\[ I(q) = I_o N(\rho - \rho_o)^2 F^2(q) \]

\[ F(q) = \frac{4}{3} \pi R^3 \left[ 3 \sin(qR) - qR \cos(qR) \right] \]
Combined SAXS and WAXS Modeling.
Quantum cubes:
Cubic 12 nm PbSe nanocrystals Assembling into a superlattice.
Self-assembled CdSe nanorod solids

Optical micrograph of self-assembled CdSe nanorods (between crossed polarizers).
III-V semiconductor nanocrystals: InP

\[ \text{InCl}_3 \cdot (\text{oct})_3 \text{P} + [(\text{CH})_3 \text{Si}]_3 \text{P} \xrightarrow{\text{TOPO-TOP}, 180-260^\circ C} \text{InP} + \ldots \]

Size-dependent evolution of absorption spectra of InP colloidal quantum dots

InP (as-prepared, weak PL) \xrightarrow{\text{HF, TOPO, } h\nu} \text{InP (strong PL)}

PL quantum efficiency \(~25-40\%\)

CdSe/CdS quantum dot - quantum rods

CdSe/CdS \( \rightarrow \) CdSe cores \( \rightarrow \) CdSe/CdS

Cd:Se = 1:1

Cd:Se = 1:3

CdSe

CdS

0° 180°

30 nm

6 nm
Luminescent II-VI nanocrystals

*Room temperature PL quantum efficiencies 50-70%*

Colloidal solutions of CdSe/ZnS core-shell nanocrystals.

CdSe/CdS core-shell nanocrystals in a polymer matrix

Single particle luminescence of CdSe/ZnS nanocrystals
**Figure 1.** Diagram of a Qdot Streptavidin Conjugate. The layers represent the distinct structural elements of the Qdot nanocrystal and are roughly to scale. As shown, Qdot quantum dots contain a semiconductor (CdSe) nanocrystal core, a semiconductor (ZnS) shell, then a polymer coat, and finally streptavidin on the outer surface.

**Figure 2.** Transmission electron micrograph of Qdot core-shell nanoparticles. Shown at 200,000X magnification. Scale bar = 20 nm.
Figure 1. Absorption spectra for bare (dashed lines) and 1–2 monolayer ZnS overcoated (solid lines) CdSe dots with diameters measuring (a) 23, (b) 42, (c) 48, and (d) 55 Å. The absorption spectra for the (CdSe)ZnS dots are broader and slightly red-shifted from their respective bare dot spectra.

Figure 2. Photoluminescence (PL) spectra for bare (dashed lines) and ZnS overcoated (solid lines) dots with the following core sizes: (a) 23, (b) 42, (c) 48, and (d) 55 Å in diameter. The PL spectra for the overcoated dots are much more intense owing to their higher quantum yields: (a) 40, (b) 50, (c) 35, and (d) 30.
Figure 5. PL spectra for a series of ZnS overcoated dots with 42 ± 10% Å diameter CdSe cores. The spectra are for (a) 0, (b) 0.65, (c) 1.3, (d) 2.6, and (e) 5.3 monolayers ZnS coverage. The position of the maximum in the PL spectrum shifts to the red, and the spectrum broadens with increasing ZnS coverage. (inset) The PL quantum yield is charted as a function of ZnS coverage. The PL intensity increases with the addition of ZnS reaching 50% at ~1.3 monolayers, and then declines steadily at higher coverage. The line is simply a guide to the eye.

Figure 6. (A) Survey spectra of (a) ~40 Å diameter bare CdSe dots and (b) the same dots overcoated with ZnS showing the photoelectron and Auger transients from the different elements present in the quantum dots. (B) Enlargement of the low-energy side of the survey spectra, emphasizing the transitions with low binding energy.
Figure 7. X-ray photoelectron spectra highlighting the Se 3d core transitions from ~40 Å bare and ZnS overcoated CdSe dots: (a) bare CdSe, (b) 0.65 monolayers, (c) 1.3 monolayers, and (d) 2.6 monolayers of ZnS. The peak at 59 eV indicates the formation of selenium oxide upon exposure to air when surface selenium atoms are exposed.

Figure 8. Transmission electron micrographs of (A) one “bare” CdSe nanocrystallite and (B) one CdSe nanocrystallite with a 2.6 monolayer ZnS shell.